

Ordered Micelle Structuring in Thin Films Formed from Anionic Surfactant Solutions

II. Model Development

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We observed the phenomenon of the stratification of thinning liquid films with both micellar solutions of anionic surfactants and solutions containing latex particles. To explain this phenomenon, we suggest that the stratification is a layer-by-layer decrease of the thickness of an ordered micellar (or latex) structure inside the film. To interpret the available experimental data for stratifying films from micellar solutions of sodium dodecyl sulfate (NaDS), a simple cell model is suggested. It permits calculation of the disjoining pressure contribution which is due to the presence of micellar structure inside the film. The micelles interact via screened electrostatic repulsion forming an ordered structure due to the restricted volume of the film. The calculated excess energy per unit area of the film exhibits a number of minima corresponding to the metastable states with micellar layers inside the film. The values of the film thickness at the metastable states were predicted by the model and agreed with the experiment. © 1989 Academic Press, Inc.

INTRODUCTION

Experiments with stratifying thin liquid films suggest an interesting possibility for gaining information about the interactions between the particles in an ordered microheterogeneous system. These films decrease their thickness step by step until a stable final state is reached. Many authors have observed and investigated the phenomenon with both foam films and emulsion films (see Part I (1)). A possible explanation of the phenomenon, suggested in some works (21, 22), is that a lamella liquid crystal structure is formed inside the stratifying film. However, as we discussed in Part I, some recent experiments with both latexes and micellar solutions of ionic and nonionic surfactants revealed for the first time that micelles or latex particles inside the film form a structure which resembles the struc-

tures observed by Hachisu *et al.* (2) for latex particles in bulk aqueous solutions. These observations form a bridge between the two phenomena: (i) ordering into microheterogeneous systems and (ii) stratification of thin liquid films.

Some indirect arguments, implying that a micellar ordering in surfactant solutions might in fact exist, can be posed as follows:

(i) The interactions between the colloid particles both in latex and in micellar solutions are due to the electrostatic repulsion between the double electric layers around the particles (the van der Waals interactions being immaterial).

(ii) Snook and van Megen (3) established theoretically that the smaller the particles, the lower the threshold concentration for the appearance of an ordered structure. Since ordering has been observed in latex solutions, more ordering should be expected to exist in

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micellar solutions (with about 100 times smaller particles).

(iii) The order-disorder phase diagram for latex solutions (Fig. 1) is similar to the stratification-nonstratification phase diagram for micellar solutions (Fig. 2). The fact that the electrolyte added in a micellar solution inhibits the stratification could then be interpreted as suppression of the micellar ordering in the solution.

The aim of this paper is to describe a theoretical model for explaining the stratification of thin liquid films formed from micellar solutions of ionic surfactants. Our analysis is based on the idea that the micelles form an ordered structure inside the film. It is also possible for a micellar structure to exist in the restricted volume of the film even when ordering is missing in the bulk solution.

Our cell model of a stratifying film (see below) is a convenient way to calculate the supplementary component of the disjoining pressure due to the micellar interactions.

MODEL OF A STRATIFYING FILM

(a) The Cell Model

Let us consider a model in which the closer neighbors of a micelle in the bulk solution oc-

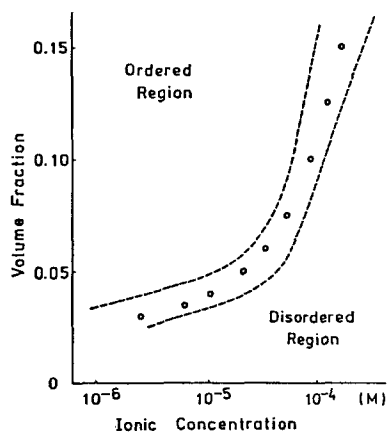


FIG. 1. The volume fraction vs concentration of added electrolyte order-disorder phase diagram for latex solutions. The dashed lines are the experimental curves of Hachisu *et al.* (2) and the circles are the theoretical points calculated by Ohtsuki *et al.* (20).

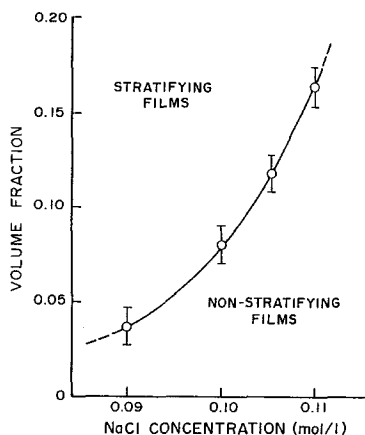


FIG. 2. The volume fraction, ϕ , vs concentration of added NaCl phase diagram for stratifying films from micellar solutions of NaDS. The Debye width of the double layers around the micelles and the dependence of the aggregation number on the NaCl concentration (1) are accounted for when calculating ϕ .

cupy the sites of a simple cubic lattice with side δ_1 . We will account only for the interactions between the first neighbors; thus, the existence (or nonexistence) of long range micellar ordering in the bulk solution will not affect our equations. In addition, let us suppose that the micellar lattice inside the film is deformed due to the interactions between the film surfaces (see Fig. 3). Thus, each micelle inside the film is situated at the center of a rectangular cell with height δ and square base of side δ_1 . In other words, the lateral distance, δ_1 , between the micelles in the film is the same as in the bulk solution, and the micellar lattice is deformed only along the thickness of the film. The quantity

$$\lambda = \delta / \delta_1 \quad [1]$$

provides a measure of the deformation. The distance between the upper (or lower) layer of micellar cells and the film surface is $h_0/2$ (see Fig. 3). The thickness of a film with n micellar layers inside is

$$h = h_0 + n\delta. \quad [2]$$

The disjoining pressure, Π , in the film can be represented as a sum of three terms:

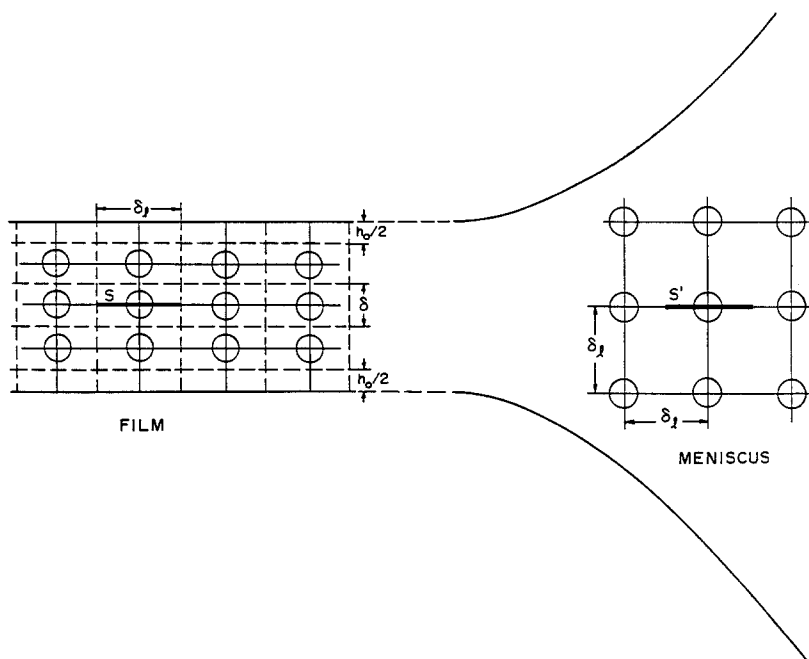


FIG. 3. Model of a film with three micellar layers inside. The deformation of the micellar lattice inside the film with respect to the nondeformed cubic lattice in the meniscus is exaggerated (the ratio $\lambda = \delta/\delta_1$ usually is not less than 0.9; see Table II).

$$\Pi = \Pi^{\text{el}} + \Pi^{\text{vw}} + \Pi^{\text{ms}}, \quad [3]$$

where Π^{el} and Π^{vw} account for the electrostatic repulsion and van der Waals attraction between the film surfaces; the presence of micellar structure inside the film gives rise to the third term, Π^{ms} . We will use the known expressions of the DLVO theory for Π^{el} and Π^{vw} ,

$$\Pi^{\text{el}} = \kappa C e^{-\kappa h}, \quad \Pi^{\text{vw}} = -\frac{A}{6\pi h^3}, \quad [4]$$

where $1/\kappa$ is the Debye length, C is a constant connected with the electric charge of the film surfaces, and A is the Hamaker constant. Our purpose below is to obtain an expression for Π^{ms} .

Using the methods of statistical mechanics, Beresford-Smith *et al.* (4-6) have established that the effective pair potential, U^{eff} , of the interaction between the particles in colloidal systems with low added electrolyte has the form of a screened Coulomb potential:

$$U^{\text{eff}} = U_0 \frac{e^{-\kappa\delta}}{\delta}, \quad [5]$$

where δ is the distance between the centers of the colloid particles. The difference between Eq. [5] and the classical Debye-Huckel expression is the manner in which the constants U_0 and κ are calculated (see the next section for more details). Equation [5] leads to an effective force

$$f = -\frac{\partial U^{\text{eff}}}{\partial \delta} = U_0 \left(\kappa + \frac{1}{\delta} \right) \frac{e^{-\kappa\delta}}{\delta}. \quad [6]$$

Let S and S' be two identical square parcels of area δ_1^2 and let S be situated inside the thin film and S' inside the bulk solution in the meniscus as shown in Fig. 3. The intermicellar interactions create pressures

$$P_m = \frac{U_0}{\delta_1^2} \left(\kappa + \frac{1}{\delta} \right) \frac{e^{-\kappa\delta}}{\delta} \quad \text{and} \\ P'_m = \frac{U_0}{\delta_1^2} \left(\kappa + \frac{1}{\delta_1} \right) \frac{e^{-\kappa\delta_1}}{\delta_1}, \quad [7]$$

exerted at the parcels S and S' , respectively. The disjoining pressure component Π^{ms} , connected with the micellar structure, is then equal to the excess pressure $P_m - P'_m$, i.e.,

$$\Pi^{ms} = \frac{U_0}{\delta_1^2} \left[\left(\kappa + \frac{1}{\delta} \right) \frac{e^{-\kappa\delta}}{\delta} - \left(\kappa + \frac{1}{\delta_1} \right) \frac{e^{-\kappa\delta_1}}{\delta_1} \right] \quad [8]$$

(see (7, 8) for the general concept of disjoining pressure). Equation [8] is visualized in Fig. 4. If one imagines that the film phase and the reference phase (the bulk liquid in the meniscus) are brought together, then an excess pressure drop, Π^{ms} , will appear at the dividing surface between them.

(b) The Excess Film Energy

The excess film energy per unit area of the film surface is equal to

$$\omega^s = -\frac{1}{2} \int \pi dh + \text{const}, \quad [9]$$

where the additive constant is to be determined from the condition $\omega^s = 0$ for the surface of the bulk solution (infinitely thick film). In our case, the disjoining pressure depends both on

the film thickness, h , and on the number, n , of the micellar layers inside the film:

$$\Pi = \Pi(h, n) \equiv \Pi_n(h). \quad [10]$$

Compare Eqs. [2]–[4] and [8]. By carrying out the integration in Eq. [9] at constant n , one obtains

$$2\omega_n^s = Ce^{-\kappa h} - \frac{A}{12\pi h^2} + n \frac{U_0}{\delta_1^2} \left[\frac{e^{-\kappa\delta}}{\delta} + \left[\left(\kappa + \frac{1}{\delta_1} \right) \delta - \left(\kappa + \frac{2}{\delta_1} \right) \delta_1 \right] \frac{e^{-\kappa\delta_1}}{\delta_1} \right], \quad [11]$$

where the additive constant has been determined from the condition $\omega_n^s = 0$ at $h \rightarrow \infty$ and $\delta \rightarrow \delta_1$ (the micellar lattice in the bulk solution is not deformed). The total excess energy per unit area of the film is

$$\omega_n = 2\omega_n^s + P_c h. \quad [12]$$

Note that for equilibrium processes ω_n equals the film tension, γ , ω_n^s equals the film surface tension, σ^f , and Eq. [12] reduces to the known Rusanov equation $\gamma = 2\sigma^f + P_c h$. See also Refs. (9, 10). Here P_c is the capillary pressure.

It is convenient to introduce dimensionless variables:

$$\tilde{h} = h/\delta_1, \quad \tilde{h}_0 = \tilde{h}_0/\delta_1, \quad \tilde{\kappa} = \kappa\delta_1, \quad [13]$$

$$\tilde{P}_c = P_c \delta_1^3/kT, \quad \tilde{\Pi}_n = \Pi_n \delta_1^3/kT, \quad \tilde{\omega}_n = \omega_n \delta_1^2/kT, \quad [14]$$

$$\tilde{A} = A/(12\pi kT), \quad \tilde{C} = C\delta_1^2/kT,$$

$$\tilde{U}_0 = U_0/(\delta_1 kT) \quad [15]$$

(k is the Boltzmann constant and T is the absolute temperature). Then in view of Eq. [1], Eqs. [2], [3], and [12] can be transformed to read

$$\tilde{h} = \tilde{h}_0 + n\lambda, \quad [16]$$

$$\tilde{\Pi}_n = \tilde{\kappa} \tilde{C} e^{-\tilde{\kappa} \tilde{h}} - \frac{2\tilde{A}}{\tilde{h}^3} + \tilde{U}_0 \left[\left(\tilde{\kappa} + \frac{1}{\lambda} \right) \frac{e^{-\tilde{\kappa} \tilde{h}}}{\lambda} - (\tilde{\kappa} + 1) e^{-\tilde{\kappa} \tilde{h}} \right], \quad [17]$$

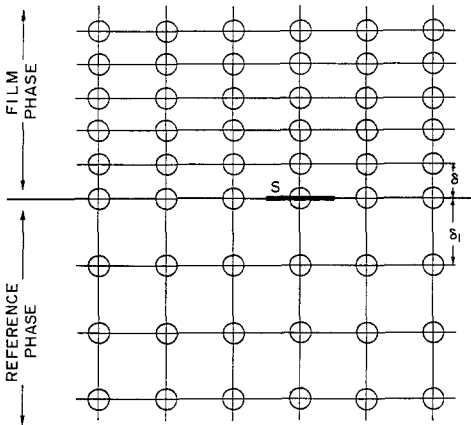


FIG. 4. The deformed micellar lattice inside the film (film phase) and the nondeformed micellar lattice in the bulk solution (the reference phase) mentally brought together. The repulsion between the micelles gives to a pressure drop (equal to Π^{ms}) at the dividing surface between the two phases.

and

$$\begin{aligned} \tilde{\omega}_n = & \tilde{C}e^{-\tilde{\kappa}\tilde{h}} - \frac{\tilde{A}}{\tilde{h}^2} + \tilde{P}_c\tilde{h} \\ & + n\tilde{U}_0\left[\frac{e^{-\tilde{\kappa}\lambda}}{\lambda} - (\tilde{\kappa} + 2)e^{-\tilde{\kappa}}\right] \\ & + \tilde{U}_0(\tilde{\kappa} + 1)(\tilde{h} - \tilde{h}_0)e^{-\tilde{\kappa}}. \quad [18] \end{aligned}$$

Equations [16]–[18] are the basic equations of the model.

At an equilibrium state the excess film energy, $\tilde{\omega}_n$, must be minimum. Hence, a necessary condition for equilibrium at a given capillary pressure, P_c , and number of micellar layers, n , is the equation

$$\left(\frac{\partial\tilde{\omega}_n}{\partial\tilde{h}}\right)_{\tilde{P}_c,n} = 0, \quad n = 0, 1, 2, \dots \quad [19]$$

Then in view of Eqs. [16]–[18] one obtains from Eq. [19] that

$$\tilde{\Pi}_n = \tilde{P}_c, \quad n = 0, 1, 2, \dots \quad [20]$$

at an equilibrium state of the film. (Equation [20] is similar to the condition for equilibrium of films without micellar structure inside.) In view of the experimental data, it should be expected that the equilibrium state with $n = 0$ (no micelles in the film) is stable, and the equilibrium states with $n = 1, 2, 3, \dots$ are metastable.

The expressions for $\tilde{\Pi}_0$ and $\tilde{\omega}_0$ in the particular case with $n = 0$ can be deduced from Eqs. [17] and [18] by using the boundary transition $\lambda \rightarrow \infty$ at finite values of \tilde{h} and \tilde{h}_0 (indeed, such a transition provides $n = (\tilde{h} - \tilde{h}_0)/\lambda \rightarrow 0$). The results are

$$\tilde{\Pi}_0 = \tilde{\kappa}\tilde{C}e^{-\tilde{\kappa}\tilde{h}} - \frac{2\tilde{A}}{\tilde{h}^3} - \tilde{U}_0(\tilde{\kappa} + 1)e^{-\tilde{\kappa}} \quad [21]$$

$$\begin{aligned} \tilde{\omega}_0 = & \tilde{C}e^{-\tilde{\kappa}\tilde{h}} - \frac{\tilde{A}}{\tilde{h}^2} + \tilde{P}_c\tilde{h} \\ & + \tilde{U}_0(\tilde{\kappa} + 1)(\tilde{h} - \tilde{h}_0)e^{-\tilde{\kappa}}. \quad [22] \end{aligned}$$

Equation [21] differs from the classical DLVO expression for the disjoining pressure by the appearance of a constant term

$$\tilde{P}_0 = -\tilde{U}_0(\tilde{\kappa} + 1)e^{-\tilde{\kappa}}. \quad [23]$$

This term is due to the presence of micelles in the bulk solution; this micellar solution is chosen to be the reference phase to account for the excess forces acting inside the film. Indeed, the boundary transition $\lambda \rightarrow \infty$ ($\delta \rightarrow \infty$) removes the micelles from the film phase as shown in Fig. 4 (without any changes in the reference phase), and the micellar repulsion then gives rise to an excess pressure, P_0 , acting on the parcel S ($P_0 = \tilde{P}_0kT/\delta_1^3$; cf. Eq. [14]). The boundary transition $\eta \rightarrow \infty$ in Eq. [21] leads to $\tilde{\Pi}_0 \rightarrow P_0$ (instead of to $\tilde{\Pi}_0 \rightarrow 0$), because this transition produces an imaginary bulk phase without micelles inside, which is obviously different from the original micellar solution (the reference phase).

RESULTS AND DISCUSSION

(a) Evaluation of the Model Parameters

As proven by Beresford-Smith *et al.* (4–6), the Debye length $1/\kappa$ of the double electric layer around a micelle must be calculated from the equation

$$\begin{aligned} \kappa^2 = & \kappa_0^2 + \kappa_{\text{counterions}}^2 \\ = & \frac{4\pi e^2 N_A}{10^3 \epsilon kT} (c_{\text{Na}} + c_{\text{DS}}). \quad [24] \end{aligned}$$

Here

$$\kappa_0 = \left[\frac{8\pi e^3 N_A}{10^3 \epsilon kT} c_{\text{DS}} \right]^{1/2} \quad [25]$$

is the reverse Debye length in the case when the contribution of the Na^+ counterions, dissociated from the micelles, is negligible (N_A is Avogadro's number and all concentrations in Eqs. [24] and [25] have dimensions of moles/liter). The thermal energy in our case is $kT = 4.1 \times 10^{14}$ ergs, the dielectric constant of water is $\epsilon = 78.5$, the values of c_{Na^+} and c_{DS^-} are given in Table I in Part I, and $e = 4.8 \times 10^{-10}$ is the electron charge in CGSE units. The dimensionless values $\tilde{\kappa}$ and $\tilde{\kappa}_0 = \kappa_0 \delta_1$ for the investigated solutions are shown in Table I. The counterion contribution to $\tilde{\kappa}$ is significant.

TABLE I
Values of the Parameters of the Model at Different Surfactant Concentrations, c_{NaDS}^a

c_{NaDS} (mole/liter)	$\bar{\kappa}$	$\bar{\kappa}_0$	h_0 (nm)	h_1 (nm)	\tilde{C}	\tilde{U}_0	P_c (Pa)	P_0 (Pa)
0.03	5.17	4.12	20.7	36.4	78.2	7.78	52.8	239
0.06	4.47	2.65	18.2	30.0	53.0	2.36	51.4	296
0.08	4.30	2.03	16.9	27.6	51.0	2.18	51.0	435
0.10	4.21	1.50	16.2	26.1	54.6	1.99	50.5	547

^a The equilibrium film thicknesses, h_0 and h_1 , are measured directly and the other parameters are calculated as explained in the text.

It should be noted that, in principle, the value of κ inside the thin film can differ from the value calculated for the bulk solution, because the micellar lattice inside the film is deformed and because the Na^+ ions dissociate from the surfaces of the film. However, reliable methods to estimate these effects do not yet exist. For this reason, we will use the bulk values of κ calculated above, with the hope that they do not differ significantly from the real values of κ inside the film.

The substitution $n = 0$ in Eq. [3] shows that $h = h_0$ for a film without micelles inside. The parameter h_0 can thus be identified with the thickness of the final stable film, assuming that it does not contain micelles. Table I lists the experimental values of the final film thickness for the different concentrations.

According to Refs. (11, 12) the Hamaker constant for water is between 3×10^{-20} and 6×10^{-20} J. We will use here the mean value $A = 4.5 \times 10^{-20}$ J for our foam films, which are composed predominantly of water.

The two coefficients, \tilde{C} and \tilde{U}_0 , are determined from the two equilibrium conditions

$$\tilde{\Pi}_0(\tilde{h}_0) = \tilde{P}_c \quad \text{and} \quad \tilde{\Pi}_1(\tilde{h}_1) = \tilde{P}_c.$$

(Cf. Eqs. [17] and [20], where $\tilde{h}_1 = h_1/\delta_1$ is the dimensionless thickness of the metastable film with one micellar layer inside. The experimental values of h_1 , along with the calculated values of \tilde{C} and \tilde{U}_0 , are presented in Table I.)

According to the conventional double layer theory, the coefficients \tilde{C} and \tilde{U}_0 are connected with the electric potentials or the surface

charges at the surfaces of the film and of the micelles, respectively. In this case, we prefer to work with surface charges rather than surface potentials, since a micellar solution does not provide a reference constant electric potential which may be regarded as a zero potential when accounting for the potential of a micelle or a film surface.

The rigorous calculations of the micellar charge from the value of U_0 are very complicated due to the presence of some nonlinear effects (5, 6). Beresford-Smith *et al.* have performed numerical calculations of U_0 for colloid particles of radius $a = 16$ nm and $\sigma = 0.031, 0.093$, and 0.261 charges per nm^2 of the surface of the particle. In our case, $\sigma = 0.25$ charges per nm^2 of the surface of a micelle, but $a = 2.4$ nm. Therefore, the nonlinear effects seem to be important, but we cannot use the numerical data in (5). Instead, we can use the approximate expression (6)

$$U_0 = \frac{(z_0 e)^2}{\epsilon} \frac{e^{2\kappa a}}{(1 + \kappa a)^2} (1 + \phi)^2, \quad [26]$$

where ϕ is the volume fraction of the micelles and z_0 is the number of charges per micelle. (Note, however, that the simple equation [26] does not account for the nonlinear effects.) From the values of \tilde{U}_0 in Table I and Eqs. [15] and [26], we calculated $z_0 = 11, 5, 4.5$, and 4 for the surfactant concentrations $c_s = 0.03, 0.06, 0.08$, and 0.10 mole/liter, respectively. As mentioned earlier, the real value of z_0 is about 18. The differences can be due both to the nonlinear effects and to the simplified character of our model.

The conventional double layer theory provides the following expression for the constant C (7):

$$C = \frac{8\pi\sigma^2}{\epsilon\kappa}; \quad [27]$$

here σ is the charge per unit area of the film surface, where a NaDS molecule occupies an area of 52 \AA^2 (1). From the value of \tilde{C} in Table I and Eqs. [15] and [27] we then calculated the degree of dissociation, α , of NaDS in the film surface monolayer. We obtained $\alpha = 4\text{--}5\%$ for each of the four investigated solutions. For comparison, the degree of dissociation of a micelle is about 27% in this concentration interval (13–15). The difference can be due to the curvature of the micellar surface, as well as to the approximations involved in both Eq. [27] and our model.

From the values of $\tilde{\kappa}$ and \tilde{U}_0 , and by using Eq. [23], one can calculate the additional pressure P_0 , created by the repulsion between the micelles in the solution. In Table I the magnitude of P_0 is compared with the value of the capillary pressure P_c . It is seen that $|P_0|$ increases when the surfactant (and the micellar) concentration is increased.

(b) Disjoining Pressure and Excess Energy Isotherms

Having evaluated the parameters of the model, one can calculate the disjoining pressure and excess energy isotherms, as well as predict the thicknesses of the metastable states with $n = 2, 3, 4, \dots$ micellar layers inside the film. From Eq. [21] one can calculate $\Pi_0(h)$ and $\Pi_n(h)$ from Eqs. [16] and [17] for $n = 1, 2, 3, \dots$. The first four disjoining pressure isotherms for 0.03 mole/liter NaDS concentration are shown in Fig. 5. It is seen that at $h \rightarrow \infty$, $\Pi_n \rightarrow P_0$. As mentioned above, this is due to the fact that each $\Pi_n(h)$ -isotherm corresponds to a given finite number, n , of micellar layers in the film, and the boundary transition $h \rightarrow \infty$ leads to an imaginary phase with zero micellar concentration. The pressure in this phase is lower than the pressure in the original micellar solution (the reference phase), because the repulsion between the micelles gives rise to the pressure P_0 ; cf. Eq. [23].

Figure 5 shows that the straight line $\Pi = P_c$ intersects all disjoining pressure isotherms. According to Eq. [20], the intersection points correspond to equilibrium states of the film

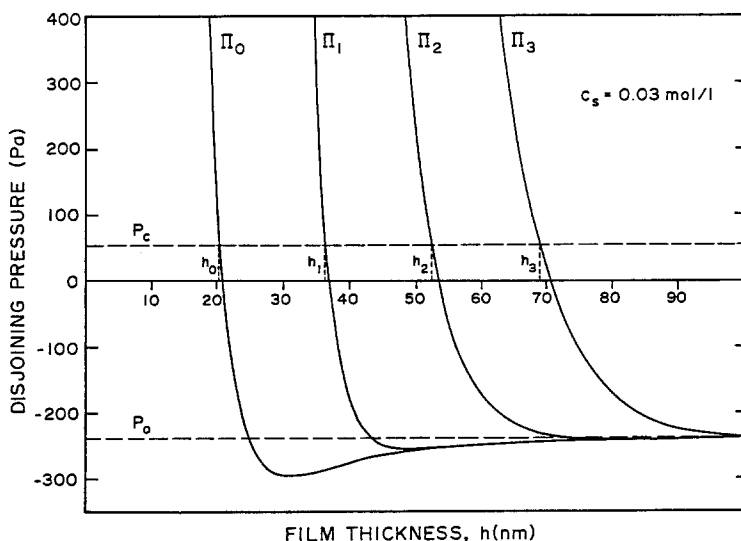


FIG. 5. Calculated disjoining isotherms $\Pi_n(h)$ for thin films with n micellar layers inside ($h_n = 0, 1, 2, 3$).

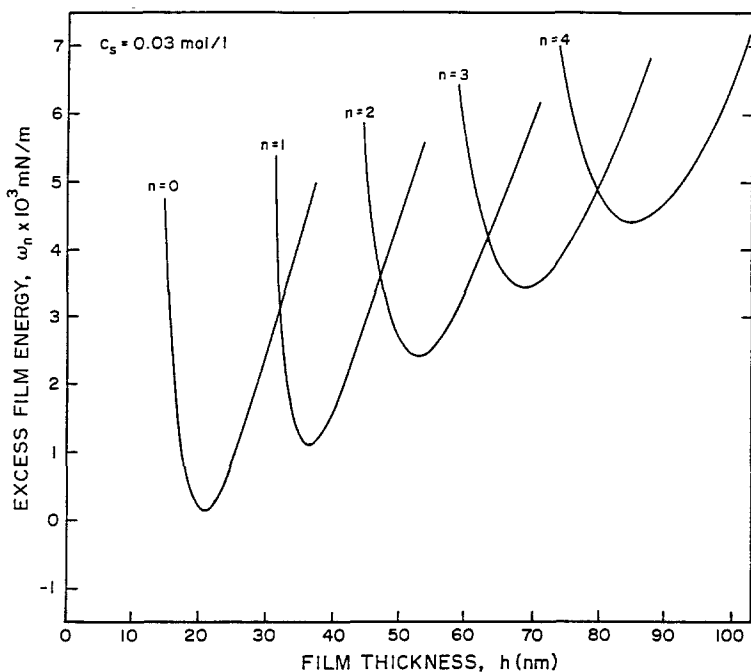


FIG. 6. Calculated isotherms of the excess energy per unit area of the film, $\omega_n(h)$, at the surfactant concentration of 0.03 mole/liter and at different micellar layers inside the film.

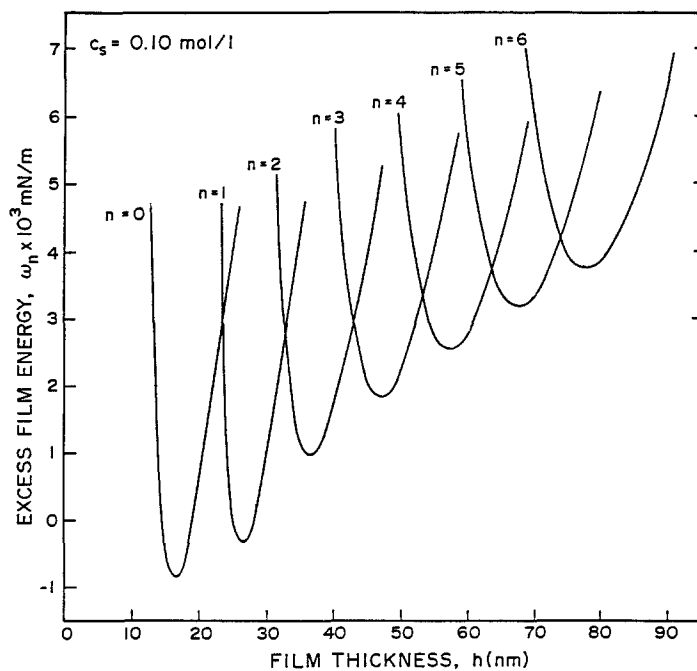


FIG. 7. Calculated isotherms of the excess energy for unit area of the film, $\omega_n(h)$, at the surfactant concentration of 0.1 mole/liter and at different micellar layers inside the film.

with thicknesses h_0, h_1, h_2, \dots . The experimental data show that the state with $n = 0$ (film without micelles inside) is stable and that the states with $n = 1, 2, 3, \dots$ are metastable. The metastable states with $n > 4$ have very short lifetimes. The step-wise character of the film thinning indicates that metastable states still exist at $n \approx 10$. An explanation of these facts is obtained from the curves $\omega_n(h)$, $n = 0, 1, 2, \dots$, calculated from Eqs. [14], [16], [18], and [22].

Figures 6 and 7 represent excess film energy curves, $\omega_n(h)$, for the lowest (0.03 mole/liter)

TABLE II

Calculated Values of the Deformation, λ , Equilibrium Film Thickness, h_n , and Equilibrium Excess Energy per Unit Area of the Film, ω_n , at Different Number, n , Micellar Layers in the Film and Different Surfactant Concentrations, c_{NaDS}

c_{NaDS} (mole/liter)	n	λ	h_n experimental (nm)	h_n calculated (nm)	$\omega_n (\times 10^3)$ (mN/m)
0.03	0	—	20.7	20.7 ^a	0.14
	1	0.946	36.4	36.4 ^a	1.09
	2	0.960	53.0	52.6	2.40
	3	0.964	67.9	68.7	3.45
	4	0.966	—	84.9	4.40
0.06				18.2 ^a	
	0	—	18.2	30.0 ^a	-0.57
	1	0.937	30.0	42.3	0.30
	2	0.956	41.3	54.6	1.56
	3	0.964	53.0	67.0	2.46
	4	0.068	64.9	79.3	3.24
0.08	5	0.969	—	—	3.95
	0	—	16.9	16.9 ^a	-0.74
	1	0.9947	27.6	27.6 ^a	-0.07
	2	0.9665	38.5	38.7	1.22
	3	0.973	49.3	49.9	2.11
	4	0.976	60.2	61.0	2.84
0.10	5	0.977	—	72.1	3.51
	1	—	16.2	16.2 ^a	-0.87
	1	0.952	26.1	26.1 ^a	-0.34
	2	0.969	35.9	36.4	0.96
	3	0.977	47.0	46.7	1.84
	4	0.980	57.9	57.0	2.53
	5	0.981	68.8	67.2	3.16
	6	0.982	—	77.5	3.74

^a These experimental values are used for calculation of the parameters of the model.

and for the highest (0.10 mole/liter) NaDS concentrations. Each curve corresponds to a given number, n , of micellar layers inside the film and the minima correspond to stable or metastable equilibrium states. The experimental and the theoretical values of the equilibrium film thickness are compared in Table II, where the respective values of the micellar lattice deformation, λ , and of the excess film energy per unit area of the film, ω_n , are also given. The theoretical and the experimental values of h at the metastable states agree. As a rule, the excess film energy, ω_0 , at the final stable state is negative. Hence, the surface energy per unit area of the film in this state is less than twice the surface energy per unit area of the bulk liquid surface, i.e., the final film state is energetically favorable. This is consistent with the fact that the final state is stable. The minima with greater values of n have higher excess energy, ω_n ; they therefore correspond to metastable states of the film.

One can notice that the curves in Figs. 6 and 7 in general resemble the shape of the oscillatory component of the repulsive hydration forces in the experiments of Israelachvili and Pashley (16) with thin films between two mica surfaces. However, these oscillations are due to the short range solvation forces (17–19) between K^+ ions; in our case the phenomenon of stratification is governed by long range screened electrostatic repulsion between micelles.

CONCLUDING REMARKS

Our analysis shows that the phenomenon of stratification of thin films formed from solutions of ionic surfactants can be explained by the existence of ordered structures of micelles inside the film. The micelles interact via long range screened electrostatic repulsion; they form ordered structures because the solution occupies a restricted volume. The simple cell model, proposed here, allows one to calculate the micellar structural component of the disjoining pressure, Π^{ms} , which is due to the presence of micellar structure inside the thin film. The total disjoining pressure also

contains terms that account for the electrostatic repulsion and van der Waals attraction between the film surfaces. A disjoining pressure isotherm, Π_n , corresponds to any given number, n , of micellar layers in the film. By integration of Π_n with respect to the film thickness, h , one can derive an expression for the excess energy, ω_n , per unit area of the film. The curves $\omega_n(h)$, $n = 0, 1, 2, \dots$, exhibit minima, which correspond to the metastable states ($n = 1, 2, 3, \dots$) and to the final stable state ($n = 0$) of the film. A step-wise film thickness transition can be interpreted as a transition from a given metastable state to the next one. The experimental values of the film thickness, h , for the equilibrium states with $n = 0$ and 1 are used to predict the values of h for $n = 2, 3, 4, \dots$, and good agreement with the experiment is obtained. The shape of the excess energy curves, $\omega_n(h)$, also reflects properly the phenomenon of stratification: the energy of the metastable states decreases with the decrease of the film thickness. The cell model can easily be improved if the real micellar lattice is not cubic, or if a new, more refined, expression for the effective pair intermicellar potential becomes available.

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REFERENCES

1. Nikolov, A. D., and Wasan, D. T., *J. Colloid Interface Sci.* **132** (1989).
2. Hachisu, S., Kobayashi, Y., and Kose, A., *J. Colloid Interface Sci.* **42**, 342 (1973).
3. Snook, I., and van Megen, W., *J. Colloid Interface Sci.* **57**, 47 (1976).
4. Beresford-Smith, B., and Chan, D. Y. C., *Chem. Phys. Lett.* **92**, 474 (1982).
5. Beresford-Smith, B., and Chan, D. Y. C., *Faraday Discuss. Chem. Soc.* **76**, 65 (1983).
6. Beresford-Smith, B., Chan, D. Y. C., and Mitchell, D. J., *J. Colloid Interface Sci.* **105**, 216 (1985).
7. Derjaguin, B. V., "Theory of Stability of Colloids and Thin Films." Nauka, Moscow, 1986. [In Russian]
8. Ivanov, I. B., and Kralchevsky, P. A., in "Thin Liquid Films" (I. B. Ivanov, Ed.), p. 49. Dekker, New York, 1987.
9. Ivanov, I. B., and Toshev, B. V., *Colloid Polym. Sci.* **253**, 593 (1975).
10. de Feijter, J. A., in "Thin Liquid Films" (I. B. Ivanov, Ed.), p. 1. Dekker, New York, 1987.
11. Visser, J., in "Surface and Colloid Science" (E. Matijevic, Ed.), Vol. 8. Wiley, Chichester, 1976.
12. Murrel, J. N., and Boucher, E. A., "Properties of Liquids and Solutions." Wiley, Chichester, 1982.
13. Sasaki, T., Hattori, M., Sasaki, J., and Nukina, K., *Bull. Chem. Soc. Japan* **48**, 1397 (1975).
14. Mysels, K. J., and Dulin, C. I., *J. Colloid Sci.* **10**, 461 (1955).
15. Vold, R. D., and Vold, M. J., "Colloid and Interface Chemistry." Addison-Wesley, London, 1983.
16. Israelachvili, J. N., and Pashley, R. M., *Nature* **306**, 249 (1983).
17. Pashley, R. M., and Israelachvili, J. N., *J. Colloid Interface Sci.* **101**, 511 (1984).
18. Ninham, B. W., *J. Phys. Chem.* **84**, 1423 (1980).
19. Hirtzel, C. S., and Rajagopalan, R., "Colloidal Phenomena—Advanced Topics." Noyes Publications, Park Ridge, NJ, 1985.
20. Ohtsuki, T., Mitaku, S., and Okano, K., *Japan. J. Appl. Phys.* **17**, 627 (1978).
21. Kruglyakov, P. M., and Rovin, I. G., "Physical Chemistry of Black Hydrocarbon Films—Bimolecular Lipid Membrane." Nauka, Moscow, 1978. [In Russian]
22. Manev, E., Sazdanova, S. V., and Wasan, D. T., *J. Dispersion Sci. Technol.* **5**, 111 (1984).
23. Reiss-Husson, F., and Luzzati, V., *J. Phys. Chem.* **68**, 3504 (1964).