

Role of Oscillatory Structural Forces for Interactions in Thin Emulsion Films Containing Micelles

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We study thin aqueous films sandwiched between two oil phases (styrene). The system is stabilized by an anionic surfactant. These films exhibit stepwise thinning (stratification), due to the presence of micellar aggregates. By means of dynamic and static light scattering, we determine the hydrodynamic diameter and the aggregation number of the micelles. Using effective micellar volume fraction, we calculate the contribution of the oscillatory structural forces to the energy of interaction between the two film surfaces. Adding also the van der Waals and the electrostatic interactions, we are able to predict the contact angles of films which contain one layer of micelles. These angles are measured by interferometry, and the obtained experimental values agree very well with the theoretical estimates. It is proved that the oscillatory structural energy dominates in the total energy of interaction. The addition of electrolyte leads to smaller contact angles. This is unexpected in view of the conventional DLVO theory, which does not consider the oscillatory structural forces. Actually, at higher salt content the effective micellar diameter (and volume fraction) decreases due to shrinkage of the electric double layer around each micelle. Therefore, the magnitude of the oscillatory structural energy diminishes, thus reducing the overall energy of attraction and the contact angle.

1. Introduction

Stepwise thinning of thin liquid films ("stratification") has been observed by many authors, both with foam and with emulsion films that contain various kinds of colloidal particles such as surfactant micelles,^{1–8} latexes,^{9,10} and protein clusters.¹¹ The universality of this phenomenon suggests the existence of a common underlying mechanism. According to the explanation put forward in ref 9, the stepwise transitions are due to layer-by-layer destruction of a colloidal crystal of spherical particles inside the film. It has been recognized^{2–9} that the stratification represents a manifestation of the structural forces whose origin is connected essentially with the volume excluded by the particles and with the overlap of the structured zones in a vicinity of the two film surfaces.

In general, whenever a surface bounds a liquid phase, ordering is induced among the particles neighboring the

wall.¹² An important prerequisite for the occurrence of such ordering is the magnitude of the surface roughness to be much smaller compared to the particle diameter.¹³ Otherwise, the structure will be smoothed out by the irregularities. For this reason, near a **liquid** interface there are oscillations in the number density of colloidal particles only if the latter are larger than ca. 5 nm. (The thermal corrugations caused by fluctuation capillary waves on fluid interfaces have a typical amplitude of 1–5 Å.) In the case of a film, the structured regions around the two opposing surfaces overlap, which gives rise to an oscillatory disjoining pressure and interaction energy.¹² The amplitude of the latter decays exponentially with the increase of the film thickness.¹²

The oscillatory structural forces have been studied theoretically by computer simulations and numerical solutions of the integral equations of statistical mechanics.^{14–20} For the sake of estimates, Israelachvili¹² proposed an analytical expression in which both the oscillatory period and the decay length of the forces were set equal to the particle diameter. This oversimplified expression proves to be unsatisfactory,²¹ as the experimental data with stratifying films give indications for

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appreciable dependence of the oscillatory period and decay length upon the particle volume fraction. To obtain a quantitatively correct formula, Kralchevsky and Denkov²¹ adopted a semiempirical approach. They analyzed the more sophisticated theory presented in ref 16 and succeeded in constructing convenient explicit equations for calculation of the oscillatory structural contribution to the disjoining pressure, Π_{osc} , and to the energy of interaction between the film surfaces, f_{osc} . In particular, f_{osc} is given by²¹

$$f_{\text{osc}} = \begin{cases} F(h) & \text{for } h \geq d \\ F(d) - (d-h)P_0 & \text{for } 0 \leq h \leq d \end{cases} \quad (1.1)$$

where the function $F(h)$ is defined as

$$F(h) \equiv \frac{P_0 d_1 \exp[d^3/(d_1^2 d_2) - h/d_2]}{4\pi^2 + (d_1/d_2)^2} \left\{ \frac{d_1}{d_2} \cos\left(\frac{2\pi h}{d_1}\right) - 2\pi \sin\left(\frac{2\pi h}{d_1}\right) \right\} \quad (1.2)$$

Here h is the film thickness, d denotes the diameter of the particles, and P_0 is their osmotic pressure in the bulk solution. It should be mentioned that eqs 1.1 and 1.2 hold only when the particles are hard spheres.²¹ The oscillatory period, d_1 , and the decay length, d_2 , are found from the following empirical relations:²¹

$$\frac{d_1}{d} = \sqrt{\frac{2}{3}} + 0.23728\Delta\varphi + 0.63300(\Delta\varphi)^2 \quad (1.3)$$

$$\frac{d_2}{d} = \frac{0.48663}{\Delta\varphi} - 0.42032; \quad \Delta\varphi \equiv \frac{\pi}{3\sqrt{2}} - \varphi \quad (1.4)$$

φ is the particle volume fraction in the bulk; the maximum content at close packing is $\varphi_{\text{max}} = \pi/(3\sqrt{2})$. In ref 21 the numerical results yielded by eqs 1.1–1.4 were tested against the outcome from the statistical mechanical theories.^{14,16,17} A reasonably good agreement was reported.

Our aim in this work is to assess quantitatively the contribution of the oscillatory structural forces to the interaction energy in stratifying emulsion films. We check the predictions of eqs 1.1–1.4 by comparison with experiment. For this purpose we measure by light scattering the hydrodynamic diameter, d_h , and the aggregation number of anionic surfactant micelles. As usual, an effective sphere diameter, d , is defined taking into account the existing ionic atmosphere around the micelles (eq 3.1 below). Thus, d and φ are determined, and f_{osc} is calculated as a function of h , using eqs 1.1–1.4. Interferometric measurements provide data for the thickness, h , of films containing different number of micellar layers. The total energy of interaction between the film surfaces, f , is represented as a sum of van der Waals, electrostatic, and oscillatory structural components:

$$f = f_{\text{vw}} + f_{\text{el}} + f_{\text{osc}} \quad (1.5)$$

All terms in eq 1.5 are calculated explicitly for films that comprise one layer of micelles. Having found a theoretical value for f , one may predict the contact angle, θ . There is a simple connection between θ and f —see, e.g., ref 22:

$$2\sigma(\cos \theta - 1) = f \quad (1.6)$$

The equilibrium interfacial tension, σ , from eq 1.6, refers to bulk phases; i.e., it is unaffected by the disjoining pressure in the film.

We compare the contact angle obtained through eqs 1.5 and 1.6 with the value measured directly from the positions of the interference fringes around the circular film. Theory and experiment are found to agree very well. In films that contain one layer of surfactant micelles the leading term in eq 1.5 is f_{osc} . This fact explains the observed decrease of θ upon addition of inorganic electrolyte. Such a trend is quite different from what one may expect if f_{osc} were not accounted for in eq 1.5. A balance which includes only van der Waals and electrostatic interactions will lead to an increase of θ with rising ionic strength.

2. Experimental Part

2.1. Materials. We used the anionic water-soluble surfactant sodium nonylphenol polyoxyethylene(25) sulfate, $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{25}\text{SO}_3\text{Na}$, supplied by the Dow Chemical Company. It will be further referred to as SNP-25S. The sample contains 0.153 mol of Na_2SO_4 per 1 mol of surfactant. The exact ratio was determined by conductivity measurements (see below). Aqueous solutions were prepared with deionized water from a Milli-Q Organex purification system (Millipore). In some cases we added inorganic electrolyte, NaCl (Merck, p.a. grade). The salt had been heated for 5 h at 450 °C prior to use, to get rid of any organic contamination. The oil phase was styrene (Merck, stabilized against polymerization). This oil solubilizes to a certain extent into the surfactant micelles present in the aqueous solution. The process of solubilization is quite slow, for that reason the experiments with thin emulsion films were carried out after allowing preequilibration. We put equal volumes of styrene and water phases in contact in a wide flask for 24 h, without stirring.

2.2. Dynamic and Static Light Scattering Measurements. We used Autosizer 4700C apparatus (Malvern Instruments, Ltd.), supplied with an argon laser (Innova, Coherent), operating at light wavelength 488 nm, and K7032 CE 8-multibit 128-channel correlator. All measurements were performed at 25 ± 0.1 °C; the samples were preliminarily filtered through 0.1 μm filter to avoid possible influence of dust particles or emulsion droplets.

By means of dynamic light scattering we determined the hydrodynamic diameter, d_h , of the **solubilized** micelles of SNP-25S. The equipment provides a value for their mass-averaged diffusion coefficient, D_0 . Then, d_h is calculated from the Stokes–Einstein relation

$$D_0 = \frac{kT}{3\pi\eta d_h} \quad (2.1)$$

where kT is the thermal energy and η is the shear viscosity of the solvent. During our measurements we did not observe any significant influence of the scattering angle upon the value of D_0 . This fact proves that the micelles are always spherical^{23–25} (and much smaller compared to the light wavelength). In other words, the micellar aggregates do not undergo transition to cylindrical ones even though oil is solubilized inside. For the sake of definiteness, we choose to use the results obtained at scattering angle of 90°.

Equation 2.1 is strictly valid for noninteracting spherical particles.²³ Since SNP-25S is ionic surfactant, the electrostatic repulsion between the micelles may be expected to affect the results for d_h considerably. Indeed, the diffusion coefficient which is actually measured, D , is known to depend on the micellar volume fraction, φ , when interactions are operative.^{24,25}

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$$D(\varphi) = D_0[1 + \lambda\varphi + O(\varphi^2)] \quad (2.2)$$

D_0 refers to a single micelle (at infinite dilution, $\varphi \rightarrow 0$), and coincides with the Stokes–Einstein coefficient, eq 2.1 (see ref 25). The parameter λ accounts for the interactions between the micelles. In principle, with $D(\varphi)$ instead of D_0 , eq 2.1 would produce an effective value for d_h which deviates from the actual size. To suppress the undesirable electrostatic repulsion, we added 0.1 M NaCl to all solutions studied by light scattering. We checked whether the effect of the intermicellar interactions was really eliminated by measuring D (viz., d_h), without oil, as a function of the surfactant concentration in the range 0.5–2 wt %. There was no detectable change of d_h within the experimental error of ± 0.3 nm. Hence, in these conditions the determined d_h is not influenced appreciably by the electrostatic repulsion, and eq 2.1 is adequate for calculation of d_h . (We could not proceed to a surfactant concentration higher than 2 wt % due to multiple scattering.)

The process of oil solubilization normally causes micellar swelling and increase of the micellar diameter. We examined the importance of that effect in our system by monitoring how d_h changed with time when the water and oil phases were brought in contact. First, 2 mL of aqueous solution of SNP-25S with concentration 1.5 or 2 wt % (plus 0.1 M NaCl) were put in the experimental cell, 2 mL of styrene were carefully added on top, without stirring, and dynamic light scattering measurements were started immediately. From 0 to 40 h d_h showed a slight increase, from 5.8 to 6.15 nm, which falls within the limits of the experimental accuracy. We accept the average value, $d_h = 6.0 \pm 0.3$ nm, that will be used for interpretation of thin liquid film results, obtained after preequilibration of the two phases for 24 h. The difference in d_h for the two concentrations, 1.5 and 2 wt %, was insignificant.

The static light scattering method consists of measuring the total time-averaged intensity of the scattered light, as a function of the particle concentration. Below the critical micellization concentration (cmc) of a surfactant the scattering is constant (and negligible), as there are only solvent molecules and solute monomers in the aqueous phase. When the cmc is reached, the scattered light intensity starts to increase and depends linearly on the concentration (within a certain range). The aggregation number of SNP-25S micelles was determined by means of a Debye plot, according to the relation²⁶

$$\frac{K(C - \text{cmc})}{R} = \frac{1}{M} + 2A_2(C - \text{cmc}) \quad (2.3)$$

Here C is the surfactant concentration (expressed in units of g/cm^3), M is the mass of one micelle (g/mol), A_2 is the osmotic second virial coefficient. The optical constant of the solution, K ($\text{mol}\cdot\text{cm}^2/\text{g}^2$), and the Rayleigh ratio, R (cm^{-1}), are defined as follows:

$$K = \frac{4\pi^2 n_0^2}{\lambda^4 N_A} \left(\frac{dn_s}{dc} \right)^2, \quad R = \frac{I_r^2}{I_0 V} \quad (2.4)$$

λ is the light wavelength in vacuum, n_0 and n_s are the refractive indices of the pure solvent and the solution, respectively, N_A is the Avogadro number; I and I_0 represent the scattered and the incident light intensities, r is the distance between the scattering volume, v , and the detector. (I_0 , r , v , and λ are constants of the apparatus.)

Figure 1 shows the Debye plot, eq 2.3, for SNP-25S in the presence of 0.1 M NaCl. We obtain a very good straight line whose intercept gives directly the mass of a micelle, $M = 36\,160$ g/mol. The cmc, required for data processing, was estimated to be about 4×10^{-4} g/cm³ by static light scattering. A possible experimental error in the determined value of the cmc is not supposed to substantially affect the results for M , because the cmc is much smaller than the concentrations at the experimental points in Figure 1. The aggregation number of SNP-25S micelles is found to be $\nu_m \approx 26$, and remains constant in the studied interval of surfactant concentrations.

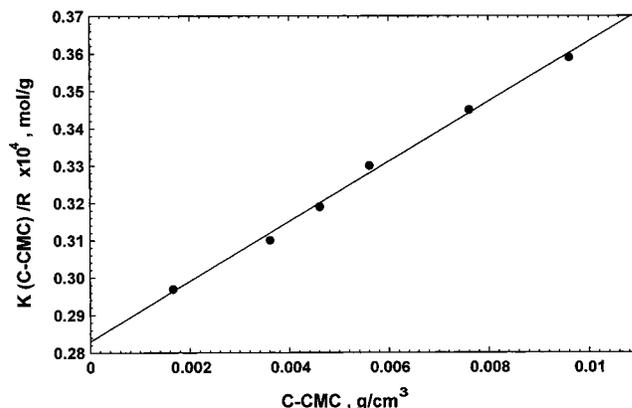


Figure 1. Debye plot (eq 2.3) of static light scattering data, obtained with aqueous solutions of SNP-25S containing 0.1 M NaCl (without oil).

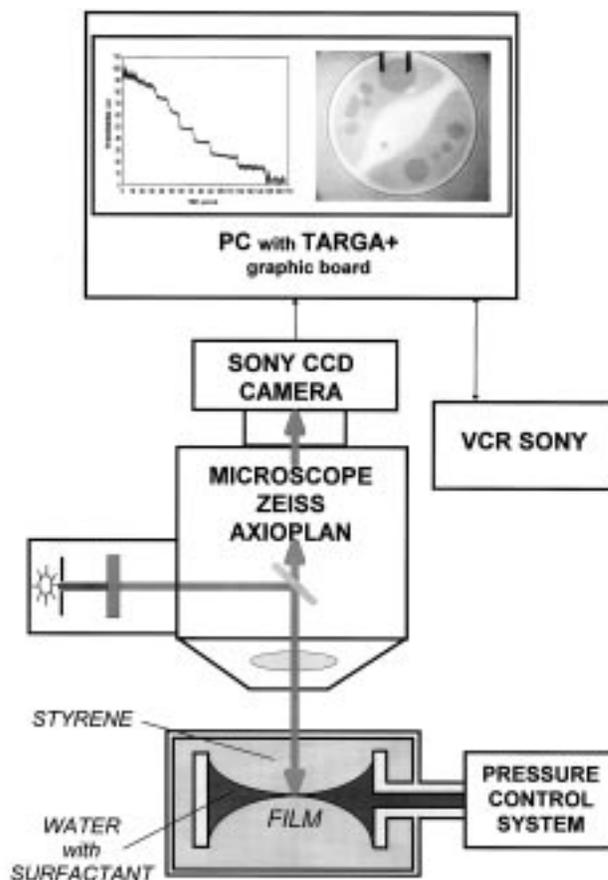


Figure 2. General scheme of the setup for microinterferometric investigation of thin emulsion films.

2.3. Interferometric Measurements with Thin Liquid Films of Emulsion Type. We work with aqueous films sandwiched between styrene phases. The experimental setup is presented schematically in Figure 2. The cell is a modification of that proposed by Scheludko and Exerowa.²⁷ Films are formed by sucking out aqueous phase from a biconcave meniscus held in a glass capillary of inner radius 1.60 mm, immersed in the oil. The cell is mounted on the table of a microscope (Zeiss Axioplan). To keep the pressure inside the meniscus constant, we use a pressure control system comprising two microsyringes and a buffer. The observations are carried out in reflected monochromatic light (with wavelength $\lambda = 546$ nm), through the optically clear cover of the cell. Images are recorded by means of a CCD camera with linear response to the incoming light (Sony, XC-

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77). We connect a VCR and a computer supplied with a Targa+ grabbing board (Figure 2). Using a special software developed by us, we register the time changes in the intensity of light which is reflected from a small fixed rectangular piece of area in the film (the size and the position of this parcel can be adjusted). The film thickness, h_f , is calculated from the following relation:²⁸

$$h_f = \frac{\lambda}{2\pi n_s} (l\pi \pm \arcsin \sqrt{\Delta}); \quad \Delta = \frac{I - I_{\min}}{I_{\max} - I_{\min}} \quad (2.5)$$

Here $\lambda = 546$ nm, l is the order of the interference, n_s is the refractive index of the liquid in the film, I is the instantaneous value of the reflected light intensity in the selected area parcel, and I_{\min} and I_{\max} denote the minimum and the maximum values of I . Thus we determine h_f during the process of film thinning.

The contact angle, θ , is found from the positions of the Newton fringes around the film periphery (see Figures 2 and 3). Black and white fringes correspond to thicknesses in multiples of $\lambda/(4n_s)$. We have made a computer program that fits the observed fringe locations with the numerical solution of the Laplace equation of capillarity. There are three parameters to be varied so as to obtain minimum deviation between the experimental data and the calculation. Our procedure is essentially the same as that used by Dimitrov et al.²⁹ The capillary pressure, the exact film radius, and the contact angle are determined from the best fit. It should be mentioned that the latter two quantities are defined at the point of intersection of the extrapolated meniscus profile with the midplane of the film.

We average the data for different radial directions in a given film, as well as for a number of films made separately. The film diameter is kept in the range from 220 to 300 μm . The error in the calculated exact radius amounts to ± 2 μm at most. The capillary pressure is typically about 75–80 dyn/cm^2 , deviating within ± 20 dyn/cm^2 . The relatively high uncertainty of the capillary pressure obtained from the numerical procedure does not however impair too much the accuracy of the contact angle determination. We normally have θ within $\sim \pm 0.1^\circ$, which is sufficient for figuring out the studied effects.

3. Results and Discussion

3.1. Determination of the Film Thickness. We performed thin film experiments with two different systems.

(A) The aqueous phase was a solution of 4.76 wt % (0.0335 M) SNP-25S, which contained also 0.00512 M Na_2SO_4 included with the surfactant; the oil was styrene. The two phases had been preequilibrated for 24 h.

(B) The same system was used as in system A, with the addition of 0.1 mol/L NaCl to the water phase.

In both cases we observed stratification and the films finally thinned down to Newton black films (NBF). The latter were stable without NaCl (system A), but ruptured within 1–2 min in the presence of NaCl (B). Figure 3 shows interference patterns of films at different moments of time during their thinning. The stepwise transitions in the thickness are clearly distinguished, as formation and expansion of darker spots occurs (darker areas are thinner). In particular, we see regions containing one and two layers of micelles (Figure 3b), and Newton black film (Figure 3c).

As an illustration, Figure 4a presents an example for the time dependence of the intensity of light, $I(t)$, reflected from a fixed small piece of film area, in the system free from excess NaCl (case A). The interferogram is further used to calculate the film thickness, $h_f(t)$ (see Figure 4b). The curve in Figure 4b has been obtained by means of eq 2.5, processing the experimental data for $I(t)$ taken from

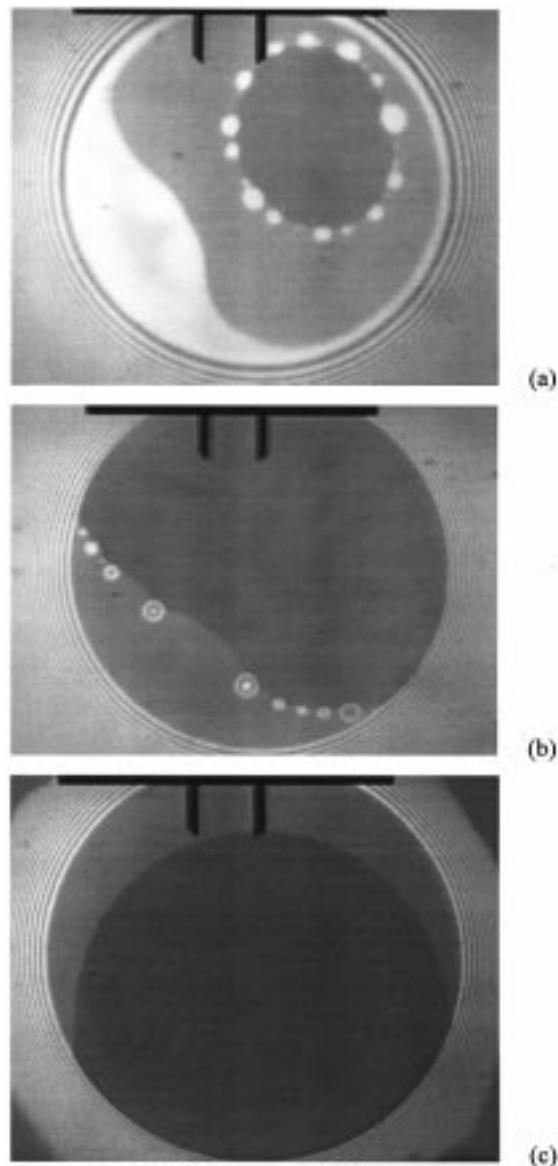


Figure 3. Interference pictures of stratifying aqueous emulsion films (observed in reflected monochromatic light). (a) Early stage of thinning of film stabilized by 3.35×10^{-2} mol/L SNP-25S. Three regions of different thickness are clearly discerned. (b) The same film a bit later. The darker part contains one layer of micelles, and the brighter one includes two such layers. Note the different contact angle (that is, the distance between the Newton fringes) around the two parts of the film compared with that in case a. (c) Film from solution of 3.35×10^{-2} mol/L SNP-25S in the presence of 0.1 M NaCl. The darker region represents a Newton black film; the brighter part comprises one layer of micelles. The reference distance between the vertical bars is 31.25 μm .

Figure 4a. This is a standard method for determination of the thickness of liquid films: The interference maximum and minimum of the reflected light intensity, I_{\max} and I_{\min} , are measured directly, from the experimental interferogram (see Figure 4a). We have $l = 0$ (eq 2.5) in the studied range of variation of the thickness. In principle, there are two alternative ways to specify I_{\min} : (i) as the intensity of the last interference minimum, which is that at thickness $\lambda/(2n_s)$ or (ii) as the intensity measured after rupturing of the film (zero film thickness). We use the latter choice to determine I_{\min} , as recommended by D. Clark.³⁰ In our case the level I_{\min} of the reflected light intensity (Figure 4a) is observed both in Newton black

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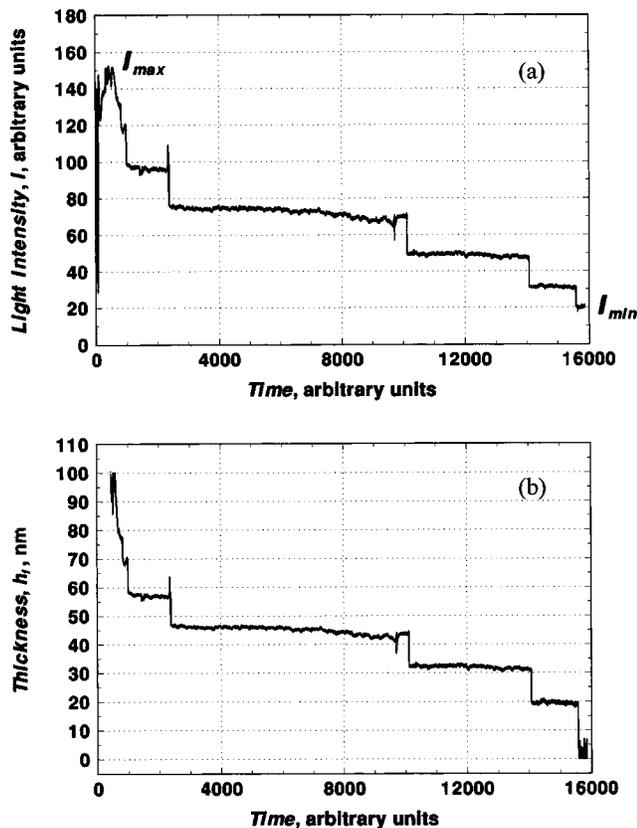


Figure 4. (a) Sample interferogram in which the directly measured reflected light intensity, $I(t)$, is plotted vs time, for a film made from aqueous solution of 3.35×10^{-2} mol/L SNP-25S (without added NaCl). (b) Stepwise change of thickness, $h(t)$, vs time, calculated from the experimental data in graph a.

films (the final stage of thinning) and without film (after rupture). It should be pointed out that very small thicknesses, close to those of the Newton black films, cannot be found with sufficient accuracy due to the imprecise measurement of I_{\min} (cf. eq 2.5). In the investigated liquid/liquid system there is appreciable scattering of light from the illuminating beam, and in addition, the signal becomes too noisy at low light intensities ($I \sim I_{\min}$). Still, at higher thicknesses the error is negligible ($I \gg I_{\min}$). For this reason, one can take the **difference** between the thicknesses of the layers, i.e., the height of the step, which will be denoted hereafter by h_m . We average the step heights from several curves such as that in Figure 4b, obtained by independent runs. The result is $h_m = 12.7 \pm 1.3$ nm for the system without excess inorganic electrolyte (A). In much the same way one finds $h_m = 10.9 \pm 1.3$ nm for the films with added NaCl (B).

Since we were not interested in the lifetimes of all metastable states, small pulse variations of the capillary pressure were applied in our experiments, so as to provoke layer expulsion, thus accelerating the transition from one state to the next one. In other words, we did not wait until the consecutive micellar layers flowed out spontaneously, with the exception of the films containing just one layer of micelles inside. The real lifetime of the latter films was only measured (see section 3.5 below). A detailed study of the lifetimes of the stratification steps was carried out by Kralchevsky et al.³¹

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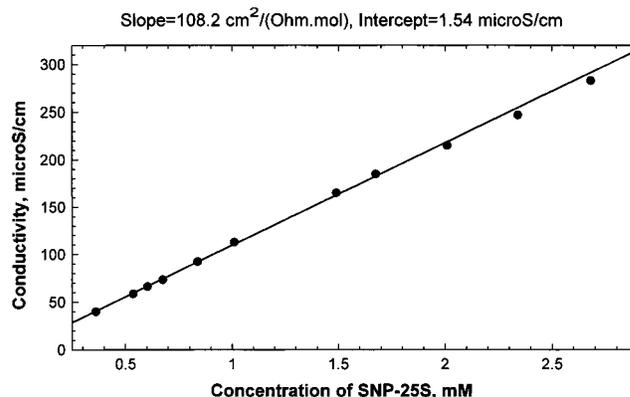


Figure 5. Measured conductivity of aqueous solutions of SNP-25S above the cmc. The system contains also Na_2SO_4 in a molar proportion of 0.153 to the surfactant.

3.2. Determination of the Effective Micellar Diameter. Now we want to calculate the oscillatory structural contribution to the energy of interaction between the film surfaces. For this purpose eqs 1.1–1.4 can be used. The micelles of the ionic surfactant SNP-25S experience electrostatic interactions, and therefore, are not exactly hard spheres. Nevertheless, they can be represented as such by taking into account the Debye counterion atmosphere.^{3,32,33} We define the effective diameter

$$d = d_h + 2\kappa^{-1} \quad (3.1)$$

which is identified with d in eqs 1.1–1.4; d_h denotes the hydrodynamic diameter of the micelles, measured by dynamic light scattering ($d_h = 6$ nm), and κ^{-1} is the Debye screening length.^{34,35}

$$\kappa^2 = \frac{8\pi e^2}{\epsilon kT} I; \quad I = \frac{1}{2} \sum_i Z_i^2 C_i^0 \quad (3.2)$$

Here ϵ is the dielectric permittivity of the aqueous solution, e is the elementary charge, and I is the ionic strength. Z_i denotes the valency of the ions i , and C_i^0 is their concentration in the bulk solution from which the film is made. The summation in eq 3.2 is carried out over all ionic species, i . κ^{-1} characterizes the width of the double electric layer around the micelles.

In principle, the parameter d_h , obtained from light scattering data and eq 2.1, may vary with the salt content (and with the ionic strength, I). The physical reason is that the dispersed micelles are involved in Brownian motion and drag to some extent their counterion atmospheres. However, the effect of changing d_h as a function of the electrolyte concentration is quite small. We can refer to the results reviewed and summarized by Mazer²⁴—see Figure 8 therein. It was experimentally established that the limiting value of the diffusion coefficient at high dilution, D_0 (eqs 2.1, 2.2), measured by dynamic light scattering of sodium dodecyl sulfate micellar solutions, remains **constant** in the range of ionic strengths between 0.025 and 0.125 M (which is our case). The

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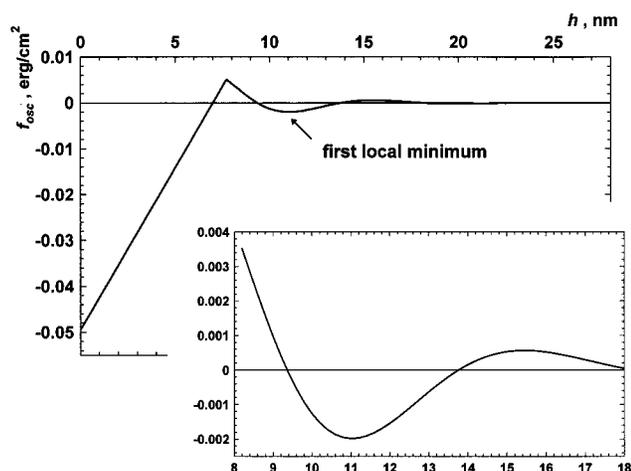


Figure 6. Calculated interaction energy due to oscillatory structural forces in a film containing 3.35×10^{-2} mol/L SNP-25S and 0.1 M NaCl (system B). The parameters are taken from Table 1. The inset shows a part of the curve at $h > d$ in a larger scale.

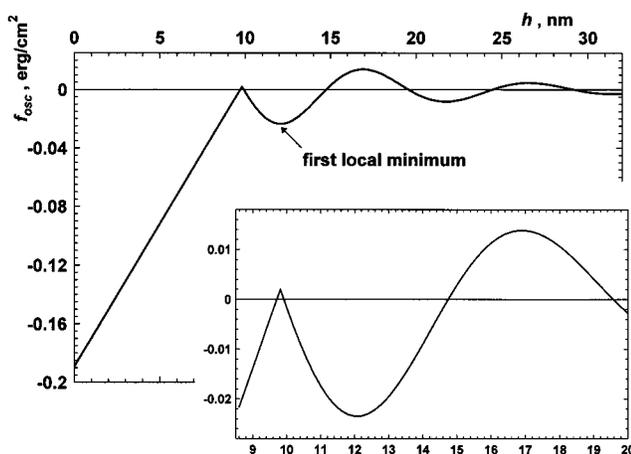


Figure 7. Calculated interaction energy due to oscillatory structural forces in a film stabilized by 3.35×10^{-2} mol/L SNP-25S (system A). The parameters are taken from Table 1. The inset shows a part of the curve at $h > d$ in a larger scale.

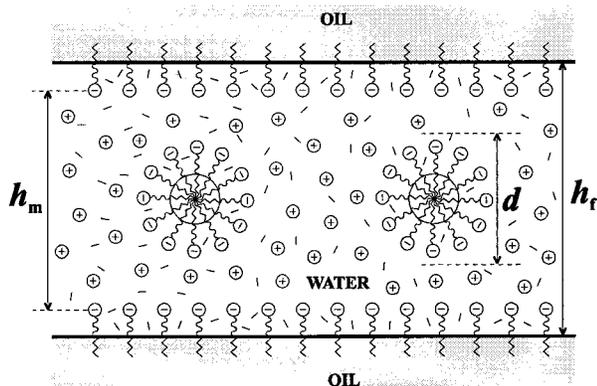


Figure 8. Sketch of aqueous film with one layer of spherical micelles inside.

absence of influence of the salt content on d_h implies that what is actually measured by dynamic light scattering is close to the real “hard-core” diameter. Moreover, the above fact of constancy of d_h may be perceived also as an indication that the aggregation number does not vary appreciably. On this basis we adopt the following assumptions: (i) in our two systems, A (without NaCl, I

= 0.02536 M) and B (containing 0.1 M NaCl, $I = 0.12536$ M), the micellar aggregation number is essentially the same; (ii) for determination of the effective micellar diameter, d (defined by eq 3.1), a possible shift in d_h of SNP-25S micelles upon addition of NaCl will be negligible compared to the effect connected with the variation of κ^{-1} (cf. eq 3.1 and Table 1). Any change of the hydrodynamic diameter, d_h , brought about either by a contribution from the counterion atmosphere or by influence of the inorganic electrolyte on the aggregation number, may be discarded as very small. Therefore, $d_h = 6$ nm will be used in both cases A and B. Direct measurement of d_h in the system A is very difficult since the experimental error rises too much due to electrostatic interactions.

3.2.1. Ionic Strength. Our systems have complex composition, so we may represent the ionic strength as a sum of contributions from several chemical components:

$$I = I_{\text{NaCl}} + I_{\text{Na}_2\text{SO}_4} + I_{\text{NaNP-25S}} \quad (3.3)$$

Simple expressions hold for the two inorganic electrolytes, NaCl and Na_2SO_4 :

$$I_{\text{NaCl}} = C_{\text{NaCl}}; \quad I_{\text{Na}_2\text{SO}_4} = 3C_{\text{Na}_2\text{SO}_4} \quad (3.4)$$

C_{NaCl} and $C_{\text{Na}_2\text{SO}_4}$ are the bulk concentrations of the respective salts ($C_{\text{NaCl}} = 0$ in the system A). The situation with the surfactant is far more complicated. The solution contains micelles, which are partially dissociated and have released some counterions (Na^+). Such solutions have been studied in the literature,^{32,33,36} and the question of how to find the ionic strength was discussed. In general, it was established that the charged micelles *should not* be included explicitly in κ and I , as they contribute in an intricate manner to the screening of the electrostatic interactions between two film surfaces or colloidal particles. Such a conclusion was made by Beresford-Smith et al.,³⁷ who considered the interactions between ionic surfactant micelles. Richetti and Kekicheff³³ fitted experimental results for the interaction force vs separation distance between adsorption layers of surfactant in solutions above the cmc. It was found that the screening length, κ^{-1} , is determined solely by the dissociated surfactant monomers and the counterions released from the micelles. Using eq 3 in ref 33, we can write for our particular system

$$I_{\text{NaNP-25S}} = \frac{1}{2}[2C_{\text{cmc}} + \alpha_m(C_{\text{NaNP-25S}} - C_{\text{cmc}})] \quad (3.5)$$

Here C_{cmc} is the critical micellar concentration of SNP-25S, $C_{\text{NaNP-25S}}$ is the total surfactant concentration, and α_m is the degree of dissociation of the micelles. The sulfate group of the *monomeric* molecule of SNP-25S is assumed to be fully ionized. With strong electrolytes such as sulfates this is a realistic conjecture and was used also by other authors (e.g., by Shanks & Franses³⁶ for sodium dodecyl sulfate).

3.2.2. Conductivity Measurements. To apply eqs 3.1–3.5, we need to know two parameters: (i) the exact proportion of Na_2SO_4 to SNP-25S in the batch surfactant sample from which all solutions were prepared and (ii) α_m . Both were determined by means of conductivity measurements at varying surfactant concentration (without added NaCl). The experiments were performed on an

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

apparatus purchased from Denver Instrument Co. (model 30), at 20 °C. As the methodology is standard, it will not be described here in details. The reader may consult refs 36 and 38, where micellar solutions were investigated by conductometry. Below the cmc of the surfactant there are only simple ions present in the aqueous phase, and the respective mobilities can be found in the literature.³⁹ The ratio $C_{\text{Na}_2\text{SO}_4}/C_{\text{NaNP-25S}}$ is constant. Then, the dependence of the conductivity, G , upon $C_{\text{NaNP-25S}}$ and $C_{\text{Na}_2\text{SO}_4}$ is represented by a straight line which passes through the zero point ($G = 0$ when $C_{\text{NaNP-25S}} = 0$ and $C_{\text{Na}_2\text{SO}_4} = 0$)

$$G = \left[\lambda_{\text{Na}^+} + \lambda_{\text{NP-25S}^-} + (2\lambda_{\text{Na}^+} + 4\lambda_{\text{SO}_4^{2-}}) \frac{C_{\text{Na}_2\text{SO}_4}}{C_{\text{NaNP-25S}}} \right] C_{\text{NaNP-25S}} \quad (3.6)$$

where, in view of the Stokes equation for the mobility, we can write

$$\lambda_i = \frac{e^2 N_A}{6\pi\eta r_i} \quad (3.7)$$

for all ions. N_A is the Avogadro number, and r_i denotes the hydrodynamic radius of the hydrated ion. The equivalent conductivity of the surfactant ions, $\lambda_{\text{NP-25S}^-}$, is estimated from eq 3.7. To assess r_i one may use an effective volume of the SNP-25S molecule in the aqueous solution (taken as the volume of the micelle, according to the measured diameter (6 nm), divided by the aggregation number, 26). Incidentally, the same approximation was applied in ref 36 (p 1796). Thus, we end up with $\lambda_{\text{NP-25S}^-} = 8.1 \text{ cm}^2/(\Omega \text{ mol})$. Besides, $\lambda_{\text{Na}^+} = 45.3 \text{ cm}^2/(\Omega \text{ mol})$ and $\lambda_{\text{SO}_4^{2-}} = 71.4 \text{ cm}^2/(\Omega \text{ mol})$ (values for 20 °C, interpolated between those for 18 and 25 °C given in refs 39). The experimental slope, obtained according to eq 3.6, is $110.86 \text{ cm}^2/(\Omega \text{ mol})$. Hence, from eq 3.6 we find the molar ratio $C_{\text{Na}_2\text{SO}_4}/C_{\text{NaNP-25S}} = 0.153$.

Above the cmc the charged micelles contribute to the conductivity.^{36,38} Therefore

$$G = [\lambda_{\text{Na}^+} + \lambda_{\text{NP-25S}^-} - \alpha_m \lambda_{\text{Na}^+} - \nu_m \alpha_m^2 \lambda_m] C_{\text{cmc}} + \left[\alpha_m \lambda_{\text{Na}^+} + \nu_m \alpha_m^2 \lambda_m + (2\lambda_{\text{Na}^+} + 4\lambda_{\text{SO}_4^{2-}}) \frac{C_{\text{Na}_2\text{SO}_4}}{C_{\text{NaNP-25S}}} \right] C_{\text{NaNP-25S}} \quad (3.8)$$

Here ν_m is the micellar aggregation number (equal to 26), and

$$\lambda_m = \frac{e^2 N_A}{3\pi\eta d_h} \quad (3.9)$$

Inserting $d_h = 6 \text{ nm}$ in eq 3.9 we get $\lambda_m = 2.727 \text{ cm}^2/(\Omega \text{ mol})$. Figure 5 presents the experimental data, plotted according to eq 3.8, above the cmc. As the concentration is quite low, the points are satisfactorily fitted by a straight line, which indicates that the interionic interactions are negligible (at least in the studied interval), and α_m remains

constant. The slope yields $\alpha_m = 0.585$ (cf. eq 3.8). We do not use the intercept because the latter cannot be determined with a good precision, due to its small value. The degree of micellar dissociation of SNP-25S is higher than that for other low molecular weight surfactants, like sodium dodecyl sulfate ($\alpha_m = 0.20\text{--}0.30$, ref 36), or dodecyltrimethylammonium bromide ($\alpha_m \approx 0.22$, ref 38). Such a fact is not surprising given the molecular structure of SNP-25S: the voluminous hydrophilic groups, containing 25 oxyethylene segments, pack loosely in the micelle.

3.2.3. Effective Micellar Volume. Having found α_m , we now calculate the ionic strength, I , and the Debye screening length, κ^{-1} , from eqs 3.2–3.5. Using eq 3.1, one estimates $d = 7.72 \text{ nm}$ in the presence of 0.1 M NaCl (system B) and $d = 9.81 \text{ nm}$ without NaCl (system A). The data are summarized in Table 1.

The effective diameter of the micelles can be determined independently from the second virial coefficient, A_2 . The latter is calculated from the slope of the Debye plot (cf. eq 2.3 and Figure 1). Our dynamic light scattering studies have proved that the micelles of SNP-25S in the presence of 0.1 M NaCl behave like spherical particles which do not experience long-range interactions. Therefore, one obtains the effective volume, V_{eff} , and the respective effective diameter, d , through the following relation:^{3,21}

$$V_{\text{eff}} = \frac{\pi d^3}{6} = \frac{1}{4} \frac{A_2 M^2}{N_A} \quad (3.10)$$

The result reads $d = 7.48 \text{ nm}$, for system B (with 0.1 M NaCl). In the frame of the experimental error of $\pm 0.3 \text{ nm}$, this value coincides with what was calculated using eq 3.1. The agreement between the two numbers, estimated by completely independent procedures, eqs 3.1 and 3.10, gives evidence for the consistency of the treatment presented above (especially, of eq 3.1, which was widely used by other authors^{2,21,32,33,40}). Besides, this also supports the conclusion that in the investigated system the micellar interactions practically do not change up to $\sim 0.0335 \text{ M}$ of surfactant. In the further discussion we shall utilize the values of d obtained from eq 3.1.

3.3. Calculation of the Oscillatory Component in the Interaction Energy. Knowing that the micellar aggregation number is 26, we obtain the concentration of particles in the solutions whose total surfactant content is $C = 4.76 \text{ wt } \%$ (0.0335 M). In combination with the results for the effective core diameter, d , this gives the volume fraction of the micelles, φ , which is also shown in Table 1. Note the big difference between the values of φ with and without NaCl. Obviously, the effect of the shrinking of the ionic atmosphere is quite essential. As long as the micelles are considered to behave as hard spheres, it is reasonable to assume that the osmotic pressure, P_0 (eqs 1.1, 1.2), can be found by means of the Carnahan–Starling formula⁴¹

$$P_0 = \rho k T \frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3} \quad (3.11)$$

where $\rho = 6\varphi/(\pi d^3)$. In fact eq 1.2, along with eq 3.11, accounts for the excess osmotic pressure in the film, which is due to the micelle–micelle and micelle–interface interactions in the restricted space between the two film surfaces. The two parameters, d_1 (the oscillatory period), and d_2 (the decay length), are readily calculated from the

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(40) Petsev, D. N.; Denkov, N. D.; Kralchevsky, P. A. *J. Colloid Interface Sci.* **1995**, *176*, 201.

(41) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.

Table 1

added NaCl, M	κ^{-1} , nm	φ	d , nm	d_1 , nm	d_2 , nm
0	1.91	0.380	9.81	9.66	9.13
0.10	0.86	0.185	7.72	8.83	3.51

Table 2

added NaCl, M	$f_{\text{osc}} \times 10^3$, erg/cm ²	$f_{\text{vW}} \times 10^3$, erg/cm ²	$f_{\text{el}} \times 10^3$, erg/cm ²	$f \times 10^3$, erg/cm ²	θ , deg	
					calcd	measd
0	-23.51	-0.37	15.47	-8.41	1.92	1.89 ± 0.08
0.10	-1.99	-0.40	0.026	-2.36	1.02	1.01 ± 0.04

empirical relations 1.3 and 1.4—see Table 1. Let us mention the pronounced difference between d and d_2 , especially at the lower micelle volume fraction, $\varphi = 0.185$.

Numerical results for $f_{\text{osc}}(h)$, obtained through eqs 1.1 and 1.2, are plotted in Figures 6 and 7, for the systems with and without added NaCl, respectively. The curves have typical shape, characterized by the existence of two regions: $0 \leq h \leq d$ and $h \geq d$. Switching over from the oscillatory regime ($h \geq d$) to the depletion ($0 \leq h \leq d$) can have important implications in view of the stability of dispersions; see refs 21 and 40 for details. In particular, the maxima can serve as potential barriers which prevent flocculation.^{21,40}

Now we can explore quantitatively the case when the film contains one layer of micelles. The molecular structure of such a film is sketched in Figure 8. As the surfactant concentration is relatively high (above the cmc), the liquid interfaces are tightly packed with amphiphile molecules. One realizes that the thickness, h , which matters for the oscillatory forces, eqs 1.1 and 1.2, should correspond to the distance between the ends of the two hydrophilic layers of polar heads anchored on the surfaces. Actually, this is h_m (Figure 8), it has been determined in the thin film experiments as the step difference in h_f upon expulsion of the micellar layer. h_f (eq 2.5) is to be perceived as the distance between the two oil/water surfaces (the full lines in Figure 8), i.e., the effective aqueous layer thickness, including the hydrated polar groups of the surfactant.

We compare the result $h_m = 10.9 \pm 1.3$ nm with the plot in Figure 6 (in the presence of 0.1 M NaCl), and similarly, $h_m = 12.7 \pm 1.3$ nm with Figure 7 (without NaCl). In both cases the experiment reveals that the film thickness is very close to the **first local minimum** of the oscillatory structural energy (despite the inevitable uncertainty in h_m). Obviously, h_m is not equal to the micellar diameter, d . This fact has been pointed out also by other authors.^{8,21} The calculated values of f_{osc} at the first local minimum are listed in Table 2 and can be identified as the oscillatory structural contributions to the respective interaction energies in our films (systems A and B).

Krichevsky and Stavans⁸ studied the heights, h_m , of the stepwise transitions in stratifying soap films containing sodium dodecyl sulfate (SDS, anionic surfactant). It was found that h_m was always considerably bigger than the hard-core micellar diameter, d_h . In addition, with rising concentration of SDS, h_m decreased. The latter effect was attributed to more pronounced electrostatic screening and shrinking of the ionic atmosphere. Such a conclusion complies with our results, as we determine lower h_m at higher electrolyte content (see above).

A matter of concern here may be the possible influence of the polydispersity of the micelles of SNP-25S. This polydispersity was measured by us, using dynamic light scattering and the method of cumulants.²³ The relative mean square deviation of D_0 was observed to be about

0.21–0.27, which does not exceed the typical values for spherical micelles of pure surfactants. Let us point out also that the height of the steps in the thickness of the stratifying films, h_m , was averaged over several interferograms registered independently. The scattering of the data for h_m is low (see above), and we find that with reasonably good accuracy the average thickness of films with one layer of micelles (h_m) lies at the first local minimum of the oscillatory energy (the latter being calculated on the basis of the **mean** micellar size, 6 nm). Such a coincidence is to be expected given the fact that the structural interaction energy prevails over the contributions of other interactions (cf. Table 2). These arguments provide evidence for the extraneous role of the micellar polydispersity in our system (the possible effect is of higher order). The case when polydisperse micelles are contained in stratifying films has recently been discussed in more detail by Nikolov and Wasan.⁴²

3.4. van der Waals and Electrostatic Components of the Interaction Energy. The final goal is to find the contact angle, θ , according to eqs 1.5 and 1.6. The van der Waals interaction energy, f_{vW} , is estimated from the relation³⁴

$$f_{\text{vW}} = -\frac{A}{12\pi h_f^2} \quad (3.12)$$

where A is the compound Hamaker constant, $A = 5 \times 10^{-14}$ erg in oil/water/oil systems.¹² Given the molecular structure of the oxyethylene chains of SNP-25S, we evaluate $h_f \approx h_m + 7$ nm (see e.g. ref 43). Then, eq 3.12 provides results for f_{vW} , which are presented in Table 2.

The electrostatic contribution to the interaction energy between the film surfaces, f_{el} , is calculated from the conventional double layer theory.^{34,35} We write

$$f_{\text{el}}(h_m) = \int_{h_m}^{\infty} \Pi_{\text{el}}(h) dh \quad (3.13)$$

with $\Pi_{\text{el}}(h)$ being the electrostatic component of the disjoining pressure.³⁴ The latter is connected with the electric potential at the midplane of the film, Ψ_0

$$\Pi_{\text{el}}(h) = kT \sum_i C_i^0 \left\{ \exp \left[-\frac{Z_i e \Psi_0(h)}{kT} \right] - 1 \right\} \quad (3.14)$$

(for the meaning of C_i^0 and Z_i , see eq 3.2). The summation in eq 3.14 is carried out over all ionic species, i . Since our films are thick, in the sense that $h_m \gg \kappa^{-1}$, it is reasonable to adopt the approximation for weak overlapping of the two diffuse ionic layers developed around the charged interfaces:³⁵

$$\Psi_0(h) \approx 2\Psi_1 \left(z = \frac{h}{2} \right) \quad (3.15)$$

Ψ_1 in the right-hand side of eq 3.15 refers to the case of a single charged plane (not a film); z denotes distance to that surface. $\Psi_1(z = h/2)$ can be determined by integration of the nonlinear Poisson–Boltzmann equation:

(42) Nikolov, A. D.; Wasan, D. T. *Colloids Surf. A* **1997**, *128*, 243.
(43) Ribeiro, A. A.; Dennis, E. A. In *Nonionic Surfactants: Physical Chemistry*; Schick, M. J., Ed.; Marcel Dekker: New York, 1987; Chapter 17, p 971.

$$\int_{\Psi_s}^{\Psi_1(z=h/2)} \frac{d\Psi}{\sqrt{\sum_i C_i^0 \{ \exp[-Z_i e \Psi / (kT)] - 1 \}}} = \sqrt{\frac{8\pi kT h}{\epsilon}} \frac{h}{2} \quad (3.16)$$

The surface potential, Ψ_s , may be large, although Ψ_0 is small. We assume that Ψ_s does not depend on the film thickness, in other words, Ψ_s is one and the same in a film and on a single interface. The final results for Π_{el} and f_{el} will not be affected by this assumption because in thick films the differences between the regimes of constant potential, constant charge, or charge regulation vanish.³⁴ Ψ_s is obtained from the boundary condition at the surface:

$$\sum_i C_i^0 \{ \exp[-Z_i e \Psi_s / (kT)] - 1 \} = \frac{2\pi e^2}{\epsilon kT} (Z_s \alpha_s \Gamma)^2 \quad (3.17)$$

Here Γ is the surfactant adsorption, α_s is the degree of dissociation of the interfacial layer, and Z_s is the valency of the adsorbed ions (-1 in our case). To determine Γ , we measured the equilibrium interfacial tension, σ , at the boundary between styrene phase and aqueous solutions of SNP-25S. The Du Nouy platinum ring method was used, and the concentration of SNP-25S was varied. From the slope of the plot of σ vs $\ln C_{\text{NaNP-25S}}$ we obtained the area per molecule to be 76 \AA^2 at complete coverage (very close to the cmc).

Next, the following algorithm was implemented numerically: (i) assuming $\alpha_s = \alpha_m$, we calculate Ψ_s from eq 3.17; (ii) for a given h , $\Psi_1(z=h/2)$ is computed according to eq 3.16; (iii) from eqs 3.15 and 3.14 we determine Π_{el} ; (iv) the integration of Π_{el} over h (eq 3.13) yields the interaction energy, f_{el} . The ions, i , which are present in our systems, are Na^+ , Cl^- , SO_4^{2-} , and NP-25S^- . The micellar surfactant solution is treated as an effective 1:1 electrolyte with concentration equal to $I_{\text{NaNP-25S}}$ (cf. eq 3.5). This is what matters for the screening of the electrostatic interactions, as shown previously by other authors.^{32,33,36,37}

The results for f_{el} are listed in Table 2. In the presence of excess NaCl (system B), f_{el} is completely negligible. On the other hand, $f_{el} = 0.01548 \text{ erg/cm}^2$ without NaCl (system A), which is comparable to $|f_{osc}|$, but is still smaller.

3.5. Total Energy of Interaction and Contact Angles. Let us now sum up the oscillatory, van der Waals, and electrostatic contributions in the interaction energy (eq 1.5). The total quantity, f (Table 2), is inserted into eq 1.6, together with the equilibrium interfacial tension, measured above the cmc, $\sigma = 7.5 \text{ dyn/cm}$. The predicted values of the contact angle, θ , are shown in Table 2. Independent measurements of θ were performed with films containing one layer of surfactant micelles (Figure 3b represents an example). The experimental results agree very well with the theoretical predictions (Table 2). Therefore, the concept of accounting for f_{osc} by means of eqs 1.1–1.4 turns out to provide a realistic description (at least for the systems under consideration).

Our microscopic observations revealed that the metastable films which included one layer of micelles inside, in the absence of NaCl (case A), lived for about 2–10 min before a Newton black film formed. On the other hand, the lifetime fell down to ~ 20 – 60 s upon addition of 0.1 M

of electrolyte (case B). Such a destabilizing effect can be interpreted in view of the circumstance that the attractive interaction energy minimum in the system A is deeper compared to the case B (Table 2).

It is important to emphasize that the oscillatory structural energy, f_{osc} , is the main component in the total interaction energy, f , cf. Table 2. This fact can be invoked to explain the influence of the inorganic electrolyte upon the value of the contact angle. The conventional theory for the interactions in thin films, developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO),^{34,35} does not consider the oscillatory structural forces, but is restricted to the van der Waals and electrostatic contributions only. In view of this theory, addition of electrolyte leads to suppression of the electrostatic repulsion between the two film surfaces. Consequently, increase of θ is expected, at rising $|f|$, $f < 0$ (cf. eq 1.6). However, exactly the opposite trend is observed experimentally (Table 2); viz., the films with 0.1 M excess inorganic salt (NaCl) have smaller contact angle compared to that without NaCl. It is evident from Table 1 that the effective micellar volume fraction, φ , falls down considerably upon addition of NaCl, due to the shrinkage of the ionic atmosphere. This turns out to be the main effect, as it brings about an order of magnitude decrease of the attraction energy, f_{osc} (Table 2). Indeed, the first minimum of the oscillatory structural energy becomes more shallow with diminishing particle volume fraction, φ : compare Figures 7 and 6.

4. Concluding Remarks

In this work we investigate stratifying emulsion films stabilized by ionic surfactant. The energy of interaction between the film surfaces is represented as a sum of van der Waals, electrostatic, and oscillatory structural contributions. Particular attention is paid to the latter, which is due to the presence of surfactant micelles. We apply the simple theoretical description, proposed recently by Kralchevsky and Denkov,²¹ to calculate the oscillatory structural energy, f_{osc} , in our films. For this purpose the diameter and the aggregation number of the micelles were measured by light scattering methods. Interferometric studies of thin emulsion films made in a capillary provide data for the stepwise transitions in the thickness, and for the contact angles. Detailed interpretation is developed for films containing one layer of micelles inside. We compare the experimental values of the contact angles with those calculated with account for the oscillatory structural energy. Good agreement between theory and experiment is observed. It turns out that the film thickness lies close to the first local minimum of f_{osc} , which corresponds to attraction between the two film surfaces. We have proved that f_{osc} dominates in the total energy of interaction. This fact explains the observed decrease of the contact angle upon addition of inorganic electrolyte. The shrinkage of the ionic atmosphere leads to decrease of the effective micellar volume fraction, φ . Consequently, the depth of the first minimum of f_{osc} diminishes by an order of magnitude.

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