

RÔLE DES FORCES STRUCTURELLES OSCILLATOIRES DANS LA STABILITÉ DES ÉMULSIONS

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ROLE OF THE OSCILLATORY STRUCTURAL FORCES FOR THE STABILITY OF EMULSIONS

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RÉSUMÉ

Nous avons étudié le crémage des émulsions huile dans eau stabilisées avec le surfactant anionique sulfate de polyoxyéthylène nonylphénol de sodium, SNP-25S. L'augmentation de la concentration du surfactant de 80 à 240 fois la concentration de micelles critique ralentit le crémage. Dans ce cas, les forces structurelles oscillatoires, dont on sait qu'elles s'accroissent lorsque la concentration du surfactant augmente, jouent un rôle significatif dans la stabilisation des émulsions en prévenant la floculation entre les gouttelettes d'huile.

Nous étudions des films aqueux fins pris en sandwich entre deux phases huileuses. Le système est stabilisé par le même surfactant, SNP-25S. Le film présente un amincissement progressif (stratification) dû à la présence d'agrégats micellaires. Nous déterminons le diamètre hydrodynamique et le nombre d'aggrégation des micelles. Nous calculons la contribution apportée par les forces structurelles oscillatoires à l'énergie d'interaction entre les deux surfaces de film. En ajoutant les interactions van der Waals et électrostatiques, nous sommes en mesure de prévoir les angles de contact des films contenant une couche de micelles. Il est prouvé que l'énergie structurelle oscillatoire occupe une position dominante dans l'énergie d'interaction totale pour les films ayant une couche de micelles. Enregistrée comme fonction de l'épaisseur, l'énergie structurelle oscillatoire atteint des valeurs maximales tenant à augmenter avec le contenu micellaire. Ces maxima peuvent faire office d'obstacles potentiels empêchant la floculation.

ABSTRACT

We study creaming of batch o/w emulsions stabilised with the anionic surfactant sodium nonylphenol polyoxyethylene-25 sulfate, SNP-25S. The increase of the surfactant concentration from 80 up to 240 times CMC leads to slower creaming. In this case the oscillatory structural forces, which are known to become more pronounced with rising surfactant concentration, play a significant role for the stabilisation of the emulsions by preventing the flocculation between the oil droplets.

We study thin aqueous films sandwiched between two oil phases, stabilised by the same anionic surfactant, SNP-25S. The films exhibit step-wise thinning (stratification), due to the presence of micellar aggregates. By means of DLS and SLS 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. It is proved that the oscillatory structural energy, f_{osc} , dominates in the total energy of interaction for films with one layer of micelles inside. When plotted as a function of the thickness, f_{osc} exhibits maxima whose height tends to increase with the micellar content. These maxima can serve as potential barriers which prevent flocculation.

1. INTRODUCTION

In the beginning of this century it was observed (1,2) that soap films decrease their thickness by several step-wise transitions. The phenomenon was called "stratification". Kruglyakov (3) reported the existence of stratification with emulsion films. Nikolov et al. (4-6) observed stratification not only with micellar surfactant solutions but also with suspensions of latex particles of micellar size. The step-wise changes in the film thickness were approximately equal to the diameter of the spherical particles, contained in the foam film (4-6). The observed multiple step-wise changes in the film thickness (Fig. 1) can be attributed to the layer-by-layer thinning of a colloid-crystal-like structure inside the film (4). Keuskamp and Lyklema (7) anticipated that some oscillatory interaction between the film surfaces must be responsible for the observed phenomenon. In fact, the step-wise transitions are manifestation of the oscillatory structural forces in the thin liquid films. Such structural forces due to surfactant micelles and microemulsion droplets were directly measured by means of a surface force balance (8). Denkov et al. (9) succeeded to freeze foam films at various stages of stratification; the electron micrographs of such vitrified stratifying films containing latex particles (144 nm in diameter) showed ordered particle array of hexagonal packing.

Oscillatory structural forces appear in two cases: (i) in very thin films of pure solvent between two smooth *solid* surfaces (10); (ii) in thin liquid films containing colloidal particles, including protein macromolecules and surfactant micelles (6). In the latter case, the structural forces affect the stability of foam and emulsion films as well as the flocculation processes in various colloids. At lower particle concentrations the structural force degenerates into the *depletion attraction* (11), which is found to destabilize various dispersions. At higher particle concentrations the structural forces stabilize the liquid films and colloids (6,12). In the special case of emulsions the maxima (Fig. 2) of the energy of the oscillatory structural forces act like barriers against the closer approach and flocculation (or coalescence) of the droplets (13). These maxima are high enough to suppress the flocculation when the particle (micelle) volume fraction is greater than c.a. 15% of the continuous phase.

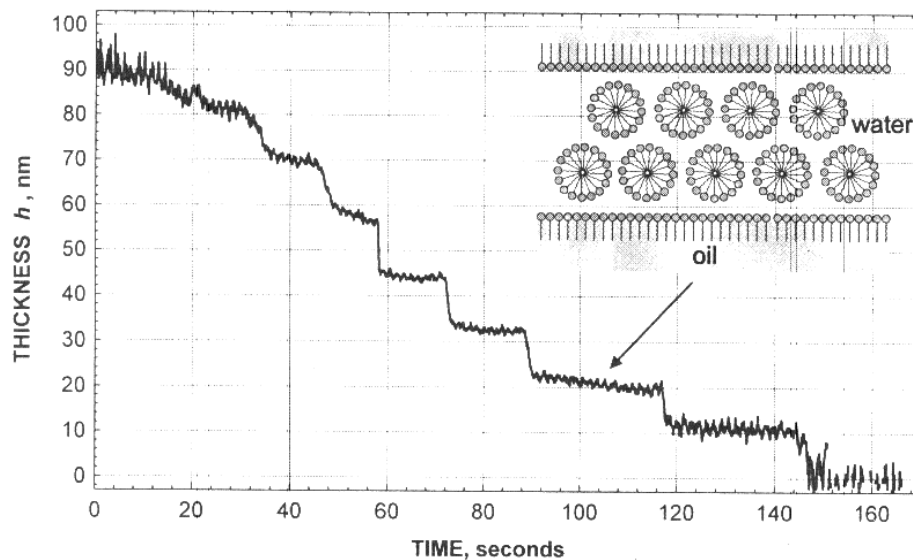


Figure 1. Experimental plot of the thickness, h , of an emulsion film vs. time. The film is formed from 33.5 mM aqueous solution of SNP-25S with 0.1 M NaCl added. The "steps" of the curve are metastable states corresponding to different number of micelle layers inside the film. The inset shows a sketch of a film containing two micelle layers, whose thickness is denoted by an arrow.

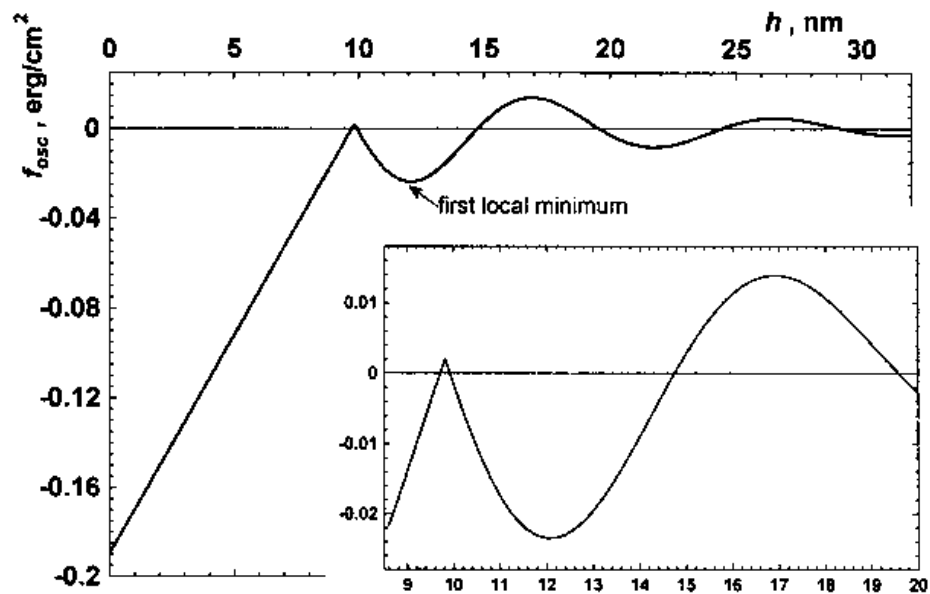


Figure 2. Plot of the oscillatory free energy, f_{osc} , vs. the film thickness, h , calculated from Eq. [4] using the parameters from Table 1, for $\phi=0.38$. The inset shows the region $8 \text{ nm} < h < 20 \text{ nm}$ in an enlarged scale.

2. RATE OF CREAMING IN EMULSIONS CONTAINING MICELLES

2.1 The experimental system. The present study is stimulated by our observation that the rate of creaming of an emulsion is markedly decreased when the concentration of the micelles in the continuous phase is increased (Fig. 3). We carried out experiments with emulsions of styrene in water. As emulsifier we used the anionic water-soluble surfactant sodium nonylphenol polyoxyethylene-25 sulfate, $\text{C}_9\text{H}_{19}\text{-C}_6\text{H}_4\text{-O-(CH}_2\text{CH}_2\text{O)}_{25}\text{-SO}_3\text{Na}$. It will be further referred to as SNP-25S. The sample contains 0.153 moles of Na_2SO_4 per one mole of surfactant. The exact ratio was determined by conductivity measurements (see ref. 14 for details). Aqueous solutions were prepared with deionized water from Milli-Q Organex System (Millipore). The styrene was product of Merck, stabilized against polymerization.

By means of dynamic light scattering (DLS) we determined the hydrodynamic diameter, d_H , of the micelles of SNP-25S. In order to suppress the undesirable electrostatic repulsion we added 0.1 M NaCl to the solutions. At these conditions the determined d_H is not influenced appreciably by the electrostatic repulsion. The solubilization of oil 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. From 0 to 40 hours d_H showed a slight increase, from 5.8 to 6.2 nm, which falls within the limits of the experimental accuracy. We accept the average value, $d_H = 6.0 \pm 0.3 \text{ nm}$, that will be used for interpretation of the results. In addition, by means of static light scattering (SLS) the aggregation number of SNP-25S micelles was found to be $v_m \approx 26$, and remained constant in the studied interval of surfactant concentrations.

2.2 Experiments with emulsions. The three curves in Fig. 3 correspond to three emulsions containing different SNP-25S concentrations in the aqueous phase: 22.3, 33.5 and 67 mM, all of them much above (from 80 up to 240 times) the critical micellization concentration, $\text{CMC} = 0.28 \text{ mM}$. Ultra Turrax 25 rotating blade homogenizer was used. The mean size of the droplets just after the homogenization was $\sim 3 \mu\text{m}$. The three emulsions were prepared at identical conditions: the initial concentration of the surfactant was 33.5 mM, the oil volume fraction was 30%. After the

preparation the three emulsions were diluted with one and the same amount of water solution containing different surfactant concentration. The final emulsions had oil volume fraction 20 % and surfactant concentrations in the aqueous phase 22.3, 33.5 and 67 mM, respectively. To study the creaming, 30 ml of such an emulsion were placed in a cylinder (with inner diameter 12 mm). The boundary between the emulsion and the aqueous phase beneath was well visible; the height of the column of the aqueous phase is plotted in Fig. 3 as a function of time. One observes diminishing of the rate of the water separation as the surfactant concentration rises (note the initial slope of the curves). Moreover, the concentrated system finally produce loosely packed cream (note the positions of the plateaus), possibly due to hampered flocculation. One can attribute the observed effects to the oscillatory structural forces. To verify this hypothesis we carried out experiments with separate emulsion films and interpreted the data by means of available theoretical expressions. As reported below, the established anomalous dependence of the film contact angle on the electrolyte concentration turns out to be an important indication of the predominant stabilizing role of the oscillatory structural forces.

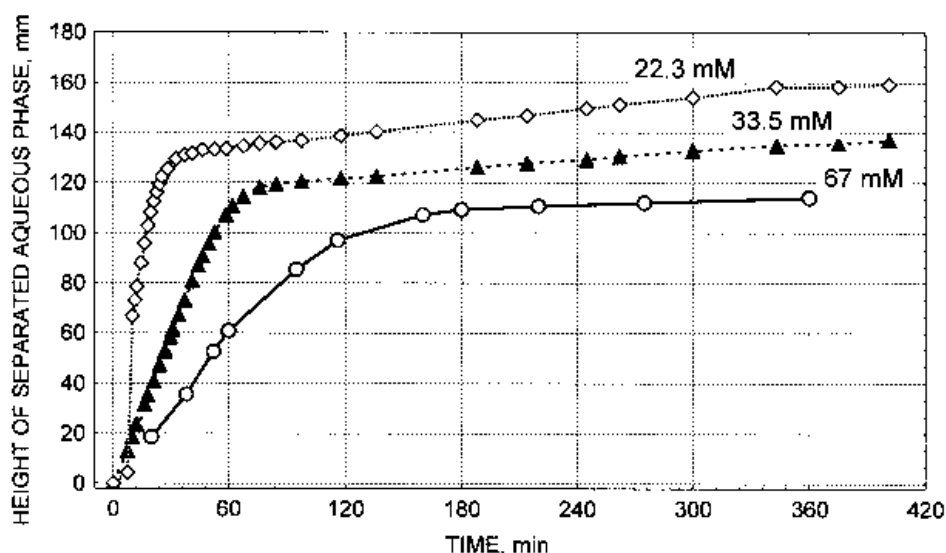


Figure 3. Plot of the height of the water column separated from a 20% styrene-in-water emulsion as a function of time. The curves correspond to different surfactant (SNP-25S) concentrations, denoted in the figure, all of them above CMC.

3. SINGLE EMULSION FILMS

3.1 Experiment. We investigated separate aqueous films sandwiched between two styrene phases. The surfactant concentration in these experiments was 0.0335 M SNP-25S, that is c.a. 120 times CMC. The styrene can be solubilised to a certain extent into the surfactant micelles present in the aqueous phase. As this process is quite slow, the experiments with thin emulsion films were carried out after 24 hours pre-equilibration of the oil and water phases. The films were formed by using the method of Scheludko and Exerowa (15), i.e. by sucking out liquid from a biconcave aqueous drop held in a glass capillary of inner radius 1.60 mm, immersed in styrene. Thus a circular film of diameter from 220 to 300 μm is formed in the center of the cell. The film is observed by a microscope in reflected monochromatic light of wavelength $\lambda=546$ nm. The film is encircled by Newton interference rings. The latter originate from the difference between the optical paths of the light beams reflected from the upper and lower surfaces of the Plateau border around the film.

The images are recorded by means of a CCD camera (with linear response to the incoming light) connected to a VCR and computer supplied with a system for image analysis. Thus from the intensity of the light reflected from the film we determine the film thickness, h (see refs. 6 and 14 for details). Fig. 1 shows h determined in this way as a function of time. Each step corresponds to a metastable state with a given number of micelle layers inside the film; the lowest value of h (on the right in Fig. 1) corresponds to a film without micelles.

In addition, by recording and processing the data for the Newton interference rings we independently determine the contact angle of the film, θ . The latter is defined as the angle subtended between the extrapolated surface of the Plateau border and the midplane of the film. Our procedure of calculations is essentially the same as that used by Dimitrov et al. (16). The accuracy of the value of θ thus determined is about ± 0.1 degrees, which is sufficient for figuring out the studied effects. For emulsion films with 0 and 0.1 M NaCl added in the aqueous phase we obtained $\theta = 1.9^\circ$ and 1.0° , respectively, at the metastable state of film containing one layer of micelles (cf. Figs. 1 and 2).

3.2 Data interpretation. To interpret the data for the independently measured thickness and contact angle of the stratifying emulsion films we employed a theoretical expression for the oscillatory structural component of disjoining pressure from ref. (17):

$$\begin{aligned} \Pi_{osc}(h) &= P_0 \cos\left(\frac{2\pi h}{d_1}\right) \exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right) & \text{for } h > d \\ &= -P_0 & \text{for } 0 < h < d \end{aligned} \quad [1]$$

where d is the diameter of the particles (micelles) considered as hard spheres; d_1 and d_2 are the period and the decay length of the oscillations which are related to the particle (micelle) volume fraction, φ , as follows (17)

$$\frac{d_1}{d} = \sqrt{\frac{2}{3} + 0.237 \Delta\varphi + 0.633(\Delta\varphi)^2}; \quad \frac{d_2}{d} = \frac{0.4866}{\Delta\varphi} - 0.420 \quad [2]$$

Here $\Delta\varphi = \varphi_{\max} - \varphi$, with $\varphi_{\max} = \pi/(3\sqrt{2})$ being the value of φ at close packing. P_0 is the particle osmotic pressure determined by means of Carnahan-Starling formula:

$$P_0 = nkT \frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3}, \quad n = \frac{6\varphi}{\pi d^3}, \quad [3]$$

where n is the particle number density. For $h < d$, when the particles are expelled from the slit into the neighboring bulk suspension, Eq. [1] describes the *depletion attraction*. On the other hand, for $h > d$ the structural disjoining pressure oscillates around P_0 , defined by Eq. [3]. It is interesting to note that in oscillatory regime the concentration dependence of Π_{osc} is dominated by the decay length d_2 in the exponent, cf. Eq. [2]. Roughly speaking, for a given thickness h the oscillatory disjoining pressure Π_{osc} increases five times when φ rises by 10% (see ref. 17 for details).

The contribution of the oscillatory structural forces to the interaction free energy per unit area of the film can be obtained by integrating Π_{osc} :

$$\begin{aligned} f_{osc}(h) &= \int_h^\infty \Pi_{osc}(h') dh' = F(h) & \text{for } h \geq d \\ &= F(d) - P_0(d - h) & \text{for } 0 \leq h \leq d \end{aligned} \quad [4]$$

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

It should be noted that Eqs. [1] and [4] refer to hard spheres of diameter d . In practice, however, the interparticle potential can be "soft" because of the action of some long-range forces. If such is the case, one can obtain an estimate of the structural force by introducing an effective hard core diameter (17)

$$d(T) = \left[\frac{3}{4\pi} \beta_2(T) \right]^{1/3}, \quad [5]$$

where β_2 is the second virial coefficient in the virial expansion of the particle osmotic pressure: $P_{osm}/(nkT) = 1 + \beta_2 n/2 + \dots$. In the case of charged particles, like ionic surfactant micelles, the following approximate expression can be also used (4,8,17)

$$d = d_H + 2\kappa^{-1}, \quad [6]$$

where d_H is the hydrodynamic diameter of the particle, determined, say, by dynamic light scattering.

In the case of 0.1 M NaCl added, using the experimentally measured hydrodynamic diameter, d_H (by DLS), and the second virial coefficient, β_2 (by SLS), we calculated the effective hard core diameter, d , by the two ways (Eqs. [5] and [6], respectively) and the results coincided in the framework of the experimental error. For the calculation of the number concentration of the micelles, n , and their volume fraction, ϕ , we used Eqs. [3] and [6].

Table 1. Data for stratifying films stabilized by SNP-25S at concentration 33.5 mM.

C_{NaCl} , M	ϕ	d nm	d_1 nm	d_2 nm	f_{el} $\times 10^3$, erg/cm ²	f_{vw} $\times 10^3$, erg/cm ²	f_{osc} $\times 10^3$, erg/cm ²	θ theor. Deg	θ exper. Deg
0	0.38	9.8	9.7	9.1	15.47	-0.37	-23.51	1.92	1.89±0.08
0.1	0.18	7.7	8.8	3.5	0.026	-0.40	-1.99	1.02	1.0±0.04

The calculated values of ϕ and d are listed in Table 1. One sees that the addition of 0.1 M electrolyte (NaCl) decreases the volume fraction of the micelles from 0.38 to 0.18 due to the shrinkage of the micelle counterion atmospheres. The period and decay length of the oscillations, d_1 and d_2 , are calculated from Eq. [2]; one sees that d_2 is markedly lower than d_1 and d , especially for the lower volume fraction $\phi=0.18$. The electrostatic and van der Waals surface free energies, f_{el} and f_{vw} , are calculated by means of the conventional DLVO-theory (see e.g. refs. 14 and 17) with Hamaker constant $A_H = 5 \times 10^{-21}$ J and area per surface charge 76 \AA^2 , whereas the oscillatory free energy, f_{osc} , is determined from Eq. [4]. For that purpose, the experimental (interferometric) thickness of films containing *one layer* of surfactant micelles has been used; corrections for the thickness of the two surfactant adsorption monolayers are taken into account when calculating f_{vw} . The theoretical and the experimental values of the contact angle, θ , of the respective films are compared in Table 1. The theoretical values of θ are calculated by means of the standard expression (cf. e.g. ref.17)

$$f = f_{el} + f_{vw} + f_{osc} = 2\sigma(1 - \cos\theta) \quad [7]$$

where $\sigma=7.5$ mN/m is the interfacial tension. One sees that the theoretical and the experimental values of θ coincide in the framework of the experimental accuracy. A theoretical plot of f_{osc} vs.

h calculated by means of Eq. [4] with the parameters taken from Table 1 is shown in Fig. 2. Note that the experimental thickness of the film containing one layer of surfactant micelles corresponds to the first minimum of f_{osc} (that at $h=12$ nm in Fig. 2). In general, the *metastable* states of the film (the steps in Fig. 1) correspond (approximately) to the *minima* of the f vs. h curve.

The numerical results in Table 1 and Fig. 2 call for some discussion. First, one sees that the contribution of the oscillatory structural force, f_{osc} , to the total surface free energy, f , is the greatest one, cf. Eq. [7]. Moreover, the magnitude of f_{osc} (the depth of the first minimum in Fig. 2) increases with the decrease of the electrolyte concentration because of the increase of the micelle effective volume fraction ϕ . As a result, the contact angle, θ , rises with diminishing of electrolyte concentration. This tendency is exactly the opposite to that in the absence of micelles, when oscillatory structural forces are missing. Hence it can be used as an indicator for distinguishing between the cases of films stabilized by the double layer repulsion and the oscillatory structural force.

4. CONCLUSION

The quantitative agreement between the theoretical and experimental values of the contact angle θ implies that the interaction in the investigated thin emulsion films is dominated by the oscillatory structural force (Table 1). Consequently, one can attribute the enhancing of the emulsion stability with the increased micelle concentration (Fig. 3) to the effect of this force. The stability of the real emulsions is governed by an interplay of surface forces (van der Waals, electrostatic, steric, oscillatory structural) and hydrodynamic ones - see ref. 18 for a recent review.

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