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STABILITY OF LIQUID FILMS IN NON-PREEQUILIBRATED EMULSIONS			155
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RÉSUMÉ

Nous étudions les films aqueux fins, pris entre des phases d'huile, en présence de surfactant soluble dans l'eau et dans l'huile. Nous étudions deux cas: (i) la surfactant est tout d'abord dissout dans la phase du film et diffuse vers l'huile, à travers les interfaces; (ii) le surfactant est dissout dans les phases d'huile et diffuse vers le film. On découvre de nouveaux effets stabilisants d'origine osmotique. Dans le cas (i), il existe une formation de cratères cyclique spontanée. L'épaisseur des films est réduite à environ 100 nm; après quoi une formation plus épaisse en forme de lentille (cratère) commence à se développer spontanément autour du centre du film. Après avoir atteint une certaine taille, le cratère s'échappe et un nouveau commence à se former. Le processus est cyclique et continue pendant des heures. Il est activé par la décharge de surfactant dans le film, qui cause un mouvement tangentiel des surfaces (effet Marangoni) et des flux de convection à l'intérieur du film. Ainsi, la phase liquide est aspirée du bord du Plateau, assurant par là-même une stabilité élevée.

On observe des films d'émulsion très épais et stables lorsque le surfactant est initialement dissout dans l'huile et diffuse vers le milieu aqueux. La circulation liquide et le transfert de masse avec le menisque adjacent se produisent à travers des canaux plus épais que le film. Cet effet est imputé à une pression osmotique excessive des micelles du surfactant, dont la concentration dans le film, saturé par le transfert en provenance de l'huile, reste supérieur à celui du bord du Plateau. Comme la diffusion des grands micelles est lente, le liquide se précipite dans le film, forcé par la pression osmotique. Le film reste épais et stable jusqu'à ce que le transfert de masse cesse, après quoi le film s'effondre.

ABSTRACT

We consider thin aqueous films between oil phases, in the presence of surfactant which is soluble both in water and in oil. Two cases are investigated: (i) the surfactant is initially dissolved in the film phase and diffuses towards the oil, across the interfaces; (ii) surfactant is dissolved in the oil phases and diffuses towards the film. New stabilising effects of osmotic origin are discovered. In the case (i) one encounters spontaneous cyclic dimpling. The films initially thin down to ~100 nm; after that a lens-shaped thicker formation (dimple) starts growing around the film center. Upon reaching a certain size the dimple flows out and a new one begins to form. The process is cyclic and keeps going on for hours. It is driven by exhausting of surfactant in the film, which brings about tangential motion of the surfaces (Marangoni effect), and convective fluxes in the film interior. Thus, liquid phase is sucked from the Plateau border, causing stabilisation.

Very thick and stable emulsion films are observed when surfactant is initially dissolved in the oil and diffuses towards the aqueous phase. Liquid circulation and mass exchange with the adjacent meniscus takes place through channels of higher thickness in the film. The effect is attributed to excess osmotic pressure of surfactant micelles whose concentration in the film, being fed up by the transfer from the oil, remains higher than that in the Plateau border. As the diffusion of the big micelles is slow, fresh liquid rushes into the film, forced by the osmotic pressure gradients. This keeps the film thick and stable until the mass transfer ceases, and then the film collapses.

1. INTRODUCTION

When two emulsion drops (of not very small size) come close to each other a thin liquid film is formed between them. The properties of this film determine to a large extent the stability of the dispersion against coalescence and flocculation (creaming). Common non-ionic surfactants, used as emulsifiers, are often soluble both in water and in oil, and are initially put in one of the phases only. Thus, immediately after formulation of the dispersion a process of surfactant redistribution starts. It can last for several hours, and even up to days, until the equilibrium is reached. Therefore, the transient phenomena associated with the mass transfer can have important practical implications.

Thin liquid films in non-equilibrium conditions were studied in the literature, and some interesting effects were disclosed. The diffusion of solutes (*not amphiphilic*) from the surrounding oil phases towards the aqueous film was found to destabilise the system [1]. This could be attributed to growth of capillary waves at the interfaces (Marangoni-Gibbs instabilities). Diffusion of *solvent* (water) across lipid bilayers, under the action of osmotic differences, proved to be vitally important for the stability of two apposed biomembranes against fusion [2]. When *surfactant* is transferred from the continuous phase (film) to the dispersed phase (oil), across the interfaces, stabilisation occurs [3]. Because the volume of the film is small, the solute concentration there falls more rapidly than in the bulk of the continuous phase. Hence, the interfacial tension is greater around the film center and smaller at the periphery and in the meniscus. As a consequence, a tensile restoring force emerges (directed from higher to lower surface pressure and adsorption). The fluid interface is set into motion, and liquid is dragged to the film center. This represents the so called Marangoni effect [3], which brings about high film stability.

The purpose of the present article is to discuss the non-equilibrium phenomena caused by the mass transfer in two opposite cases: (i) surfactant is initially dissolved in the film phase and diffuses towards the oil, across the fluid boundaries; (ii) surfactant is first dissolved in the oil, and then it diffuses to the film.

New effects of stabilisation were discovered in both cases. Evidence is found for existing correlation with the properties of batch emulsions.

2. SPONTANEOUS CYCLIC DIMPLING

2.1. Description of the phenomenon

Vetev et al. [4] studied the role of the surfactant redistribution by making experiments with aqueous films between xylene phases. The films were formed in a glass capillary (method of Scheludko and Exerowa [5]), microscopic observation in reflected monochromatic light was carried out. The interference pattern of Newton fringes was recorded. The pictures allow reconstruction of the interfacial profiles at any moment of time, and in this manner the evolution of the film can be monitored.

When polyoxyethylene (20) sorbitan monolaurate (Tween 20) is initially dissolved in water, it starts diffusing to the oil as soon as the two phases are brought in contact in the experimental cell. This engenders a fascinating phenomenon of spontaneous cyclic dimpling, which is illustrated in Figure 1. After reaching a certain thickness (typically, above 100 nm), the films stop thinning. Then, a lens-like thicker formation (dimple) spontaneously forms around the film center, and starts to grow gradually. Upon reaching a certain size, the dimple becomes unstable and quickly flows out to the Plateau border. Almost plane-parallel film is left behind. Immediately afterwards a new dimple starts to grow, and so on. The process is cyclic and usually keeps going for hours. The driving force was proved to be the surfactant mass transfer [4]. When the latter ceases, the film quickly thins down and eventually ruptures.

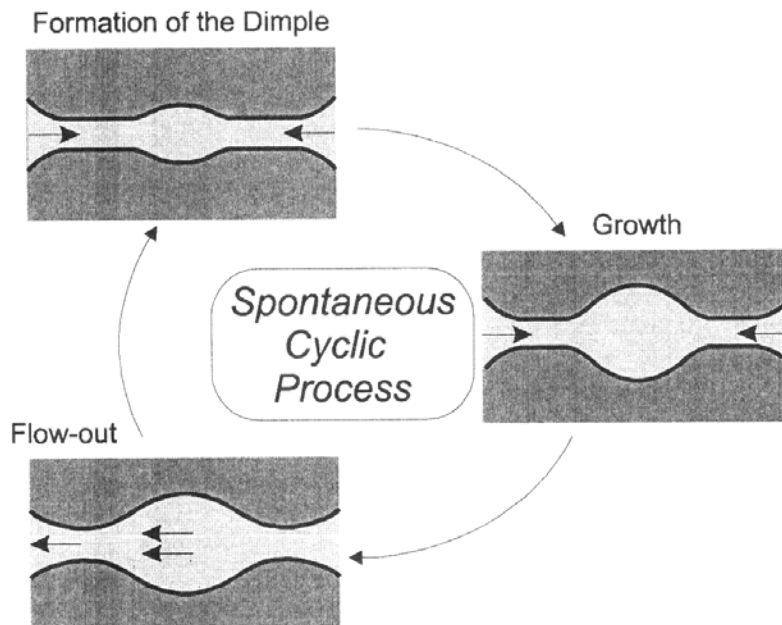


Fig. 1. Development of the spontaneously oscillating dimple during one cycle.

It should be pointed out that the films containing such dimples are rather thick (up to ~ 300 nm), even in the presence of a large amount of added inorganic electrolyte (e.g., 0.1 mol/l NaCl). In these conditions no other sources of stabilisation are operative, except purely hydrodynamic ones.

A clear distinction must be made between the phenomenon described above and the so-called hydrodynamic dimple. The latter appears only when the film is thinning, and is not connected in any respect with mass transfer through the phase boundaries. The film surfaces are curved under the combined action of the pressure gradients and the viscous friction (see e.g. Ref. [6]). At a certain stage of thinning the hydrodynamic dimple irreversibly disappears and the film becomes plane-parallel.

2.2. Hydrodynamic theory for the process of dimple growth

The problem can be solved in lubrication approximation: $h(r,t) \ll R$ (the local thickness is everywhere much smaller than the film radius). Low Reynolds number is assumed, and the time derivatives in the Navier-Stokes equation are discarded (the physical quantities depend on time implicitly, through $h(r,t)$). The pressure and the radial velocity in the bulk of the film have the form:

$$p = q(r,t), \quad v_r = \frac{1}{2\eta} \frac{\partial q}{\partial r} (z^2 - h^2) + u. \quad (1)$$

On the upper interface, S, with equation $z = h(r,t)$, one has

$$v_r = u, \quad v_z = \frac{\partial h}{\partial t} + u \frac{\partial h}{\partial r} \quad \text{at S.} \quad (2)$$

The shape is governed by

$$\frac{\partial h}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (rhu) = \frac{1}{3\eta r} \frac{\partial}{\partial r} \left(rh^3 \frac{\partial q}{\partial r} \right), \quad (3)$$

where the unknown functions $u(r,t)$, $\partial q/\partial r$ are to be determined from the boundary conditions at S .

From the side of the oil the characteristic thickness of the layer where the velocity changes significantly is $\delta_v \approx \sqrt{\nu_0 \tau} \sim 1 \text{ cm} \gg h$, which means negligible viscous stresses (here ν_0 is the kinematic bulk viscosity, and τ is the time scale of the tangential motion, $\tau \sim 100$ sec). In the presence of low molecular weight surfactants the effect of the **interfacial** viscosity may be shown to be immaterial. Then, the tangential stress boundary condition on S reads:

$$h \frac{\partial q}{\partial r} = \frac{\partial \sigma}{\partial r}, \quad (4)$$

where σ is the interfacial tension. We have also the normal stress balance

$$-\frac{\partial q}{\partial r} = \frac{\partial}{\partial r} \left[\frac{\sigma}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) \right] \quad \text{at } S. \quad (5)$$

From the equation of convective diffusion in the bulk one can determine the surfactant flux towards the interface, j_f . Bearing in mind that the film is being continuously fed with fresh liquid from the Plateau border, it is reasonable to work at small perturbations of the concentration in the dimple, $c(r,z,t)$, with respect to that in the volume of the aqueous phase, c_0 . We also suppose fast adsorption, and hence

$$\Gamma = \Gamma_0 + \left(\frac{\partial \Gamma}{\partial c} \right)_0 (c - c_0), \quad \sigma = \sigma_0 + \left(\frac{\partial \sigma}{\partial c} \right)_0 (c - c_0) \quad \text{at } S, \quad (6)$$

where the subscript "0" means that the respective quantity refers to equilibrium at c_0 . The surface mass balance reads:

$$\frac{\partial \Gamma}{\partial t} + \nabla_{II} \cdot (\Gamma \mathbf{v} - D_s \nabla_{II} \Gamma) = j_f - j_0. \quad (7)$$

Here Γ denotes the adsorption, \mathbf{v} is the velocity on S , and j_0 is the constant mass flux to the oil phase. With typical values of the physical parameters it can be demonstrated that the molecular surface diffusion (characterised by D_s) is negligible compared to the convective transport. Then, by combining Eqs. (1)-(7) we arrive at the final form of the differential equation which describes the shape of the dimple:

$$\frac{\partial h}{\partial t} + \frac{1}{3\eta r} \frac{\partial}{\partial r} \left\{ r h^3 \frac{\partial}{\partial r} \left[\frac{\sigma_0}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) \right] \right\} = \frac{j_0}{2\Gamma_0} \frac{\partial}{\partial r} (r^2 h) \quad (8)$$

The following boundary conditions have to be satisfied: at $r=0$ (in the center of the film) $\partial h/\partial r$ and $\partial^3 h/\partial r^3$ should be zero; at the rim, $r=R$, the thickness remains fixed (equal to h_0), and $\partial h/\partial r$ vanishes. The initial condition is arbitrary, so that one may even use experimentally determined profiles to start the computation from. Eq. (8) is solved numerically, with sufficiently small time step in order to reach convergence.

Now, it is desirable to compare the theoretical results with experiment. For that purpose we have studied aqueous films made from solution of the non-ionic surfactant nonyl-phenol polyglycol (40) ether, 3.23 %wt., in the presence of 0.1 mol/l NaCl. The oil phase was styrene. The time evolution of the dimples was monitored taking shapes at different moments. From the positions of the Newton fringes, and from the condition for interference of the light beams reflected from the film, we restored the interfacial profiles. The first measured profile was inserted as initial condition for the calculation, and the subsequent ones were fitted. The result is presented in Fig. 2. Apparently, the obtained agreement is very good. There is only one free parameter to be varied, j_0 , whose value is $j_0 = 9.13 \times 10^{12} \text{ cm}^{-2} \cdot \text{sec}^{-1}$ for the particular case shown in Fig. 2.

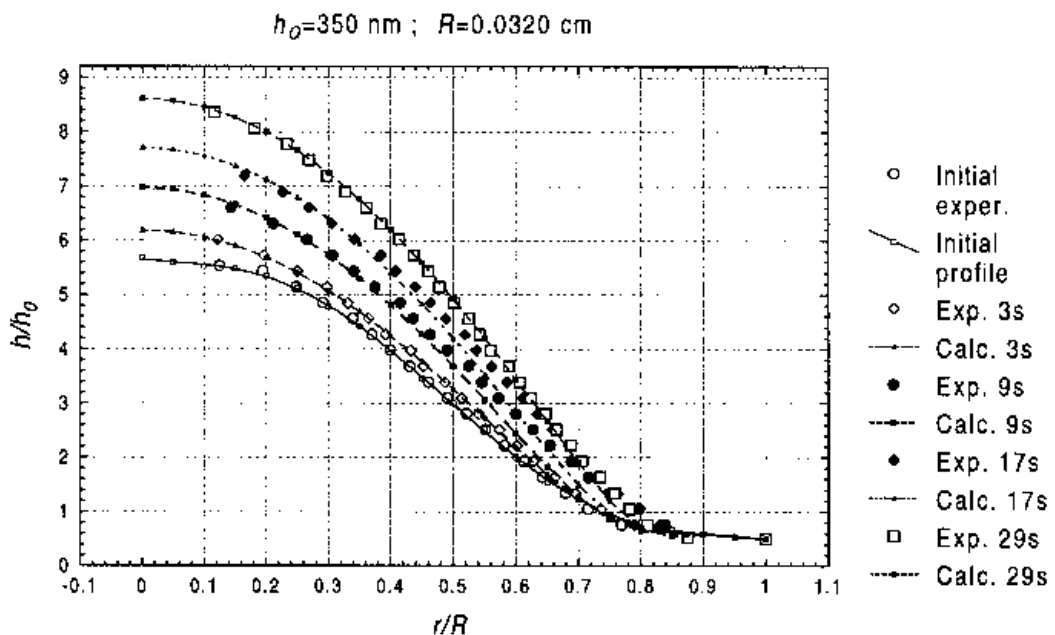


Fig. 2. Fit of experimental data for the profile of the growing dimple.

The theory in its present form does not account for the *cyclic* nature of the processes, it always gives a stationary final shape. Such is indeed observed, when the surfactant fluxes are not very intensive. If they are, however, the steady state cannot be reached because instabilities occur in the film and the dimple is expelled at some critical size. After that a new dimple appears and that is how the oscillations come about. More detailed investigation of the flow properties can be found in Ref. [7]. Vortices are proved to exist in the interior of the film, and the pressure attains quite low values close to the periphery.

If we summarise the explanation of the phenomenon, the major role should be attributed to the Marangoni effect, connected with interfacial tension gradients (cf. Eq. (4)). The surface convection, that is, the inward flow along the interfaces, directed from the meniscus to the film, provides a continuous supply of new surfactant. As a fluid element moves to the film center, it continuously loses surfactant because the latter goes to the oil. Therefore, the adsorption (Γ) decreases and σ rises with diminishing values of the radial coordinate, r . The gradients of σ set the fluid interface into motion. Due to the viscous friction, liquid is dragged into the film, thus feeding the dimple.

3. OSMOTIC STABILISATION BY NON-EQUILIBRIUM DISTRIBUTION OF SURFACTANT MICELLES

We carried out experiments with aqueous films, in the presence of non-ionic surfactant (Tween 20) which was initially dissolved in the oil phase and afterwards diffused to the film, across the interfaces. The water contained 0.1 mol/l NaCl. The films remained thick (above 100 nm) and stable, until the equilibrium distribution of surfactant was reached (that took a time period up to 48 hours). Then, the films thinned down and ruptured. We observed specific dynamic pattern, connected with intensive liquid circulation and exchange of mass in lateral direction between the film and the Plateau border (see Figure 3).

We varied the surfactant concentration in the oil phase. It turned out that the effects emerge in a threshold manner: below a certain "critical" concentration (3.3×10^{-4} mol/l Tween 20) there is no stabilisation at all.

Experiments were performed with films whose phases contained given amount of surfactant (C_0 , per unit volume), *before* being put in contact with the oil. The stabilising effect and the general pattern of the process were the same for $C_0=0, 1, 10, 100$, and even $500 \times \text{CMC}$. C_0 represents a background concentration, evenly distributed both in the film and in the meniscus during the experiment. Such a big surfactant content does not influence the film stability, which indicates that only the *excess* concentration in the film with respect to the meniscus is important.

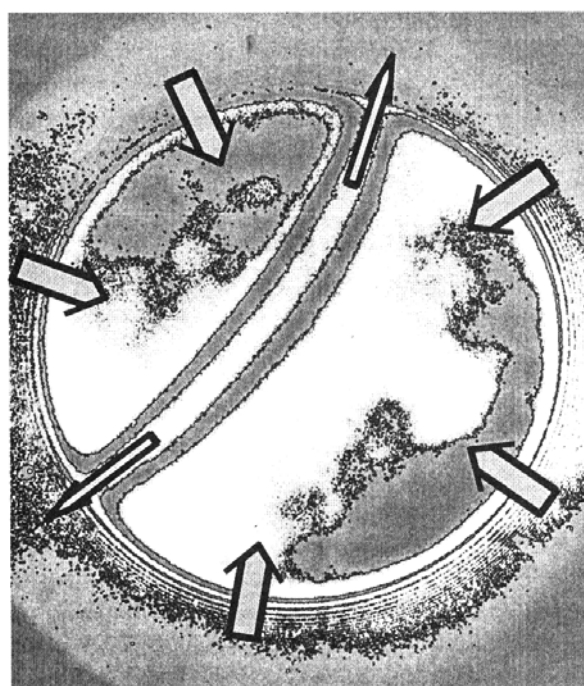


Fig. 3. Sketch of the liquid fluxes in a film with a channel

These findings may be rationalised in view of the following explanation: As the surfactant diffuses through the interfaces, its concentration in the aqueous film gradually increases. Two types of solute species exist in the water phase: single molecules (monomers) and micellar aggregates. The diffusion of the monomers is fast, and they are uniformly distributed in the aqueous phase. The local monomer concentration in the film cannot increase above the CMC because the individual molecules, after crossing the oil/ water boundary, quickly form micelles. The characteristic time of micellisation is typically of the order of milliseconds [8], i.e., it is much smaller than the time scale of the hydrodynamic motion (~minutes). As the monomer concentration in the water remains constant, the diffusion flux coming from the oil cannot stop until the equilibrium distribution is reached. The thin and broad film gets enriched with micelles, whose concentration in the voluminous Plateau border remains low (the Brownian diffusion of the big aggregates is slow). The increased osmotic pressure of *micelles* in the film engenders convective fluxes of liquid: Material is sucked from the meniscus, and after saturation with surfactant it rushes out through the channels of higher thickness (Fig. 3). Some numerical estimates that support the above physical interpretation can be found in Ref. [9].

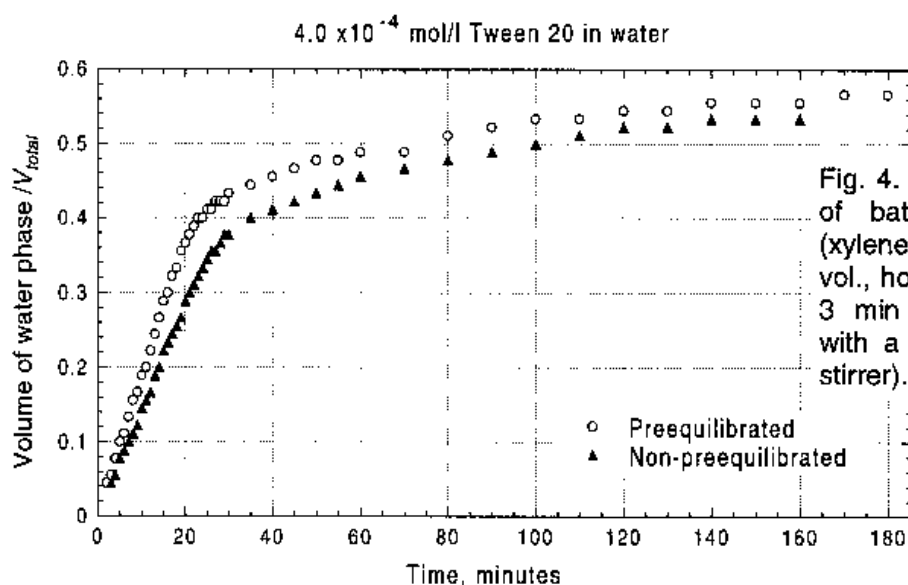


Fig. 4. Creaming rate of batch emulsions (xylene-in-water, 30% vol., homogenised for 3 min at 2000 rpm with a rotating blade stirrer).

Figure 4 illustrates the role of the mass transfer for the stability of a real dispersion. The volume of the aqueous (lower) phase, separated from two emulsion samples (of 50 ml each), preequilibrated and non-preequilibrated, is plotted vs. time. No coalescence was noticed, but the creaming was well pronounced. Both systems initially contained 4×10^{-4} mol/l Tween 20 in water, in the preequilibrated emulsion there was also 5.7×10^{-5} M surfactant in the oil (the distribution coefficient is ~ 7.0 in favour of water). Fig. 4 shows that the system with mass transfer is more stable, despite the lower total surfactant content. Still, the effect is not very large, probably because the droplets are small (with diameter $\sim 5 \mu\text{m}$), and only slightly deformed, so that the films have a small size.

4. CONCLUSIONS

It is proved that the non-equilibrium effects connected with surfactant redistribution lead to high thickness and stability of aqueous films sandwiched between two oil phases. When the mass transfer is from the film to the oil, spontaneous cyclic dimpling occurs. In the opposite case (transfer from the oil to the film) there is osmotic stabilisation due to the maintained excess of surfactant micelles in the film with respect to the Plateau border.

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