Abnormal Thickness and Stability of Nonequilibrium Liquid Films

O. D. Velev,[1] T. D. Gurkov,[1,*] I. B. Ivanov,[1] and R. P. Borwankar[2]

[1]*Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia,*
1 James Boucher Avenue, Sofia 1126, Bulgaria
[2]*KRAFT General Foods, Inc., Technology Center, 801 Waukegan Road, Glenview, Illinois 60025*
(Received 21 November 1994)

Thick and very stable aqueous films between oil phases are obtained in systems where surfactant diffuses across the interfaces, towards the film. An osmotic pressure difference exists between the film interior and the surrounding aqueous meniscus. This is due to surfactant aggregates (micelles); it pushes the film surfaces apart, giving rise to intensive liquid circulation and exchange of mass with the meniscus.

When two deformable colloid particles, like emulsion drops (or living cells), are pressed against each other, a thin planar aqueous film is formed between their interfaces (or membranes). The interactions between the film surfaces determine the stability and the behavior of the colloid system. Over many years the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1], based on electrostatic and van der Waals interactions, has provided a guideline for understanding the colloid systems. In the past two decades sources of interactions which are out of the scope of the DLVO theory have been revealed [2–8]. In this work we report experimental observations of aqueous emulsion films containing nonionic surfactant soluble both in water and in oil. The films exist under nonequilibrium, but quasistationary conditions, when diffusion of the surfactant from the oil towards the film phase takes place. The abnormally large thickness of these films cannot be explained by either the DLVO theory or another kind of treatment involving only direct surface forces.

We carried out experiments on water films formed in a modified cell of Scheludko and Exerowa [9,10] (Fig. 1). Earlier we have reported a pronounced dependence of the lifetimes of emulsion films with mass transfer upon the direction of solute transport [11]. We have also observed a fascinating cyclic phenomenon of spontaneous formation of dimples (thicker lenslike formations) inside aqueous films in the case of surfactant diffusion out of the films towards the adjacent oil phases [12]. The present Letter reports the complementary case when the nonionic surfactants are initially dissolved in the surrounding oil and diffuse through the interfaces towards the water film (Fig. 1).

In a previous paper [13] we have shown that similar, but equilibrated emulsion films, containing $0.1M$ NaCl, spontaneously thin down in a few minutes to a very thin "black" film (thickness ~ 10 nm), and rupture. In complete agreement with DLVO theory, this follows from the lack of any long-range repulsion between the surfaces, since the electrostatic interaction is suppressed by the presence of $0.1M$ of electrolyte.

Quite unexpectedly, in our current investigations at the same NaCl concentration, when the surfactant is initially dissolved in the oil, neither black film formation nor rupture is observed. On the contrary, the films retain a large thickness (above 100 nm—colored films in reflected white light). They follow a specific dynamic behavior connected with intensive liquid circulation and exchange of mass in the lateral direction between the film and the plateau border (Fig. 1). This is a long-term transient effect driven by the emulsifier redistribution between the phases. The phenomenon is qualitatively explained here in view of the excess osmotic pressure of surfactant aggregates (micelles) inside the film, compared to that in the surrounding meniscus. We have established that once the mass transfer ceases (this usually take a time period over 48 h, during which most of the surfactant is transferred from the oil to the water), the films do not remain thick but thin down to black films and rupture.
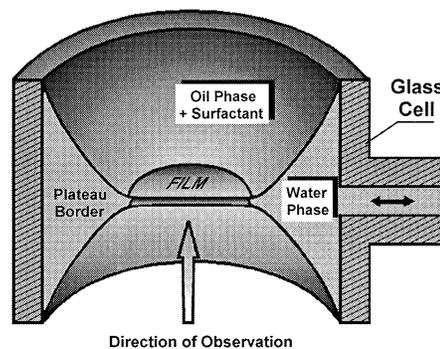

FIG. 1. Schematic presentation of the experimental cell. The films are formed by sucking out aqueous phase from a biconcave meniscus held in a capillary [9,10]. This simulates the formation of an aqueous film between two oil droplets pressed against each other. The microscopic observations in reflected monochromatic light ($\lambda = 546$ nm) allow reconstruction of the profile of the film surfaces on the basis of the recorded interference picture. The films have a circular shape and diameters between 100 and 500 μm. The inner diameter of the most often used capillary is 2.98 mm. Note that the film and cell dimensions in the figure are not to scale.

The experiments were carried out with the nonionic surfactants Tween 20 [polyoxyethylene (20) sorbitan monolaurate] and Tween 60 [polyoxyethylene (20) sorbitan monostearate] from ICI Specialties. The oil phase into which the surfactants were dissolved was xylene (isomeric mixture, p.a. grade). The water was extracted from a Millipore Milli-Q unit. The electrolyte concentration inside the aqueous phase was adjusted at $0.1M$ by the addition of NaCl (Merck), heated at $450\,°C$ for 4 h prior to use. All studies were performed at $22 \pm 0.2\,°C$.

The increased film thickness and stability are coupled with a specific dynamic pattern of the surfaces. One observes formation of "channels" of higher thickness connecting two points of the film periphery (Figs. 2 and 3). The channels emerge as a consequence of the intensive hydrodynamic circulation of liquid. In order to follow the fluid motion, the trajectories of some small particles attached to the surfaces of the film were traced. It was witnessed that the aqueous phase is sucked from the plateau border through the film periphery, and after getting saturated with surfactant this phase is thrown out through the channels. The average time for evolution of a channel is about 10–15 min, after which another one appears at a different location.

In order to clarify the physical mechanism by which the surfactant diffusion across the film surfaces gives rise to liquid motion and high stability, we carried out experiments with varying surfactant concentration in the xylene and in the water phases.

(i) Varying the emulsifier concentration in the xylene phase. Effects occur in a threshold manner: stable films of abnormally high thickness are formed only above a certain concentration of film stabilization (CFS). Below CFS, the films thin down to black films and rupture within about

3 min. The value of CFS is $3.3 \times 10^{-4}M$ for Tween 20 and $5.3 \times 10^{-4}M$ for Tween 60.

(ii) Varying the evenly distributed emulsifier concentration in the water phase. We prepare aqueous films whose phases contain *beforehand* a certain amount of surfactant. During the experiment this initially dissolved surfactant will be evenly distributed both in the film and in the surrounding meniscus. It was established that the effect of stabilization and the general pattern of the process are the same when the aqueous phase initially contains no surfactant as well as when 1, 10, 100, or even $500C_{mic}$ (critical micelle concentration C_{mic}) of Tween 20 is initially dissolved in the water ($C_{mic} = 5 \times 10^{-5}M$ for Tween 20 [14]). Thus, the film stability is transiently increased by a comparatively small amount of surfactant in the oil phase (CFS), while being unaffected by the presence of a large quantity of evenly distributed surfactant in the film. These striking findings can hardly be explained by the conventional concepts [15].

The experimental observations can be rationalized by assuming that the nonelectrostatic stabilization of very thick aqueous films originates from the higher osmotic pressure of *surfactant aggregates* (micelles) in the film compared to that in the surrounding plateau border (Fig. 4).

The surfactant is initially dissolved in the oil. Because of diffusion through the oil/water interfaces, its concentration in the aqueous film gradually increases. Two types of surfactant species exist in the water phase: single molecules (monomers, not shown in the figures) and aggregates (micelles). 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 critical micelle concentration (CMC) because the surfactant molecules, after crossing the oil/water boundary, quickly form micelles. The characteristic micellization time is typically of the
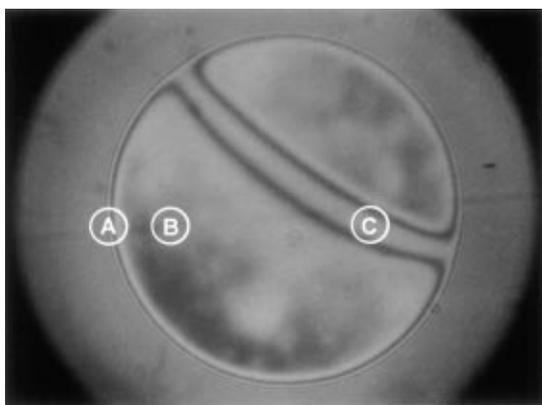

FIG. 2. Interference picture of a typical film with a "channel" formed in an experiment with $5 \times 10^{-4}M$ of Tween 20 in the xylene phase. The letters in the figure denote (A) the transition region between the film and the plateau border; (B) approximately plane-parallel film portion; and (C) a channel of higher thickness. Each transition from bright to dark film area or vice versa corresponds to a change of thickness of 102 nm. The film diameter is 450 μm.
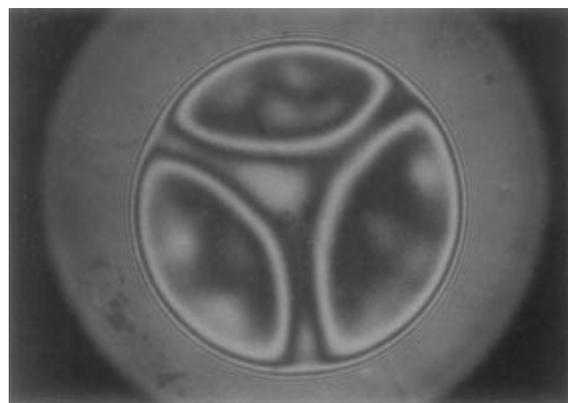

FIG. 3. A multichannel pattern registered when the surrounding oil phase initially contains $6.6 \times 10^{-4}M$ Tween 60. In the case of Tween 60 the phenomenon of formation of channels is more pronounced. The diameter of the film is 430 μm.
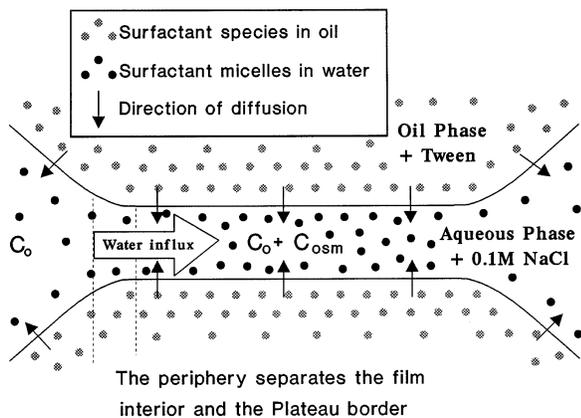
FIG. 4. Schematic presentation of the origin of the increased osmotic pressure between the film surfaces.

order of milliseconds to seconds [16,17]; i.e., it is much smaller than the time scale of the hydrodynamic motion (~10 min). As the *monomer* concentration in the water remains constant, the diffusion flux coming from the oil cannot stop until the equilibrium distribution ratio of the surfactant between the phases is reached.

The thin and broad film gets enriched with surfactant micelles, while their concentration in the surrounding voluminous plateau border remains low, as the diffusion of the big micellar species is slow and the diameter of the film is much larger than its thickness. The origin of the increased osmotic pressure and of the consequent influx of liquid is the excess micellar concentration inside the film, C_{osm} (Fig. 4). An analysis of the film behavior from the viewpoint of this osmotic model allows us to explain the results from the experiments with varying surfactant concentration.

(i) The liquid circulation will occur in a threshold manner only above a certain excess concentration, C_{osm}. The osmotic pressure could force the film surfaces apart when it becomes higher than the capillary pressure P_{cap}, which presses these surfaces against one another:

$$P_{osm} = kTC_{osm} \geq P_{cap}$$

(compare with Refs. [7], [15], and [18]; kT is the Boltzmann constant multiplied by the temperature).

(ii) As osmotic phenomena are driven only by the difference of the solute concentrations between the film and the meniscus, the value of the evenly distributed concentration of micelles, C_0 (Fig. 4), should not affect the process even though C_0 can be orders of magnitude higher than C_{osm}.

The conclusions from the osmotic model are supported by simple estimations. The capillary in our cell is $P_{cap} \sim 70$ dyn/cm^2. The osmotic pressure becomes equal in magnitude to P_{cap} at an estimated excess concentration $C_{osm} = 1.7 \times 10^{15}$ cm^{-3} which corresponds to ~$3C_{mic}$ of surfactant dissolved in the film (assuming for Tween 20 an aggregation number of 30 [14]). The determined

CFS in the oil is equivalent to $6C_{mic}$ (if the same amount of surfactant were dissolved in water). When the micellar concentration C_{osm} rises further, so the engendered osmotic pressure rises above the capillary pressure, $P_{osm} > P_{cap}$, the liquid outside the film will be able to push the two surfaces apart and flow in. The circulations starts, and we believe that in this way the channels are generated. A comprehensive theory of the effect should connect the surfactant diffusion flux with osmotic pressure gradients and resulting hydrodynamic fluxes inside the film. This is a typical nonequilibrium thermodynamics problem—a similar phenomenon of the coupling of fluxes is encountered, e.g., in the well-known Bénard convection cells, driven by heat transfer across liquid layers [19].

In our case we can expect the liquid circulation to be more intensive when the deviation from equilibrium is higher. This can be achieved by increasing the film diameter (which may lead to higher C_{osm}). Indeed, when the diameter is smaller than 200 μm, only one thicker segment near the film periphery is observed (no channels exist). On increase of the film size over 300 μm, the thicker region expands and prolongs to form a channel.

The time dependence of the film behavior (above CFS) also confirms the decisive role of the concentration ingredients. Initially, the dynamics of the liquid circulation in the film is very intensive. About 2 h after the loading of the cell, the processes become appreciably retarded, and reach a quasistationary state. No changes in the thickness are noticed up to 5–6 h. Further, within a time period over 24 h, the mass transfer effects gradually decelerate. Moreover, the thickness of the approximately plane-parallel film areas between the channel and the periphery is found to decrease slowly. This thickness reaches values in the range of 30–60 nm (grey color), when a spot of black film appears at a certain point. The thickness of the black film, measured earlier in equilibrated systems, is 12 ± 3 nm [13]. Once a black spot has appeared, it expands, pushing the liquid out of the film. This process usually takes 2–3 min and after that rupture occurs. When a film is formed more than 48 h after the loading of the cell, it is no longer stable but thins down within 10–15 min, undergoes transition to black film, and ruptures. Apparently, the driving force for the mass transfer has already been exhausted at that time, which drastically reduces the stability.

The repulsive osmotic forces witnessed by us could happen to be a source of stabilization of emulsions or biological dispersions under nonequilibrium conditions.

*To whom correspondence should be addressed.

[1] B. V. Derjaguin, *Theory of Stability of Colloids and Thin Films* (Plenum Press, New York, 1989).

[2] H. K. Christenson, J. Fang, B. W. Ninham, and J. L. Parker, J. Phys. Chem. **94**, 8004–8006 (1990).

[3] J. N. Israelachvili and R. M. Pashley, Nature (London) **300**, 341–342 (1982).

[4] J. N. Israelachvili and H. Wennerström, J. Phys. Chem. **96**, 520–531 (1992).

[5] H. de Hek and A. Vrij, J. Colloid Interface Sci. **84**, 409–422 (1981).

[6] P. A. Kralchevsky and V. N. Paunov, Colloids Surfaces **64**, 245–264 (1992).

[7] P. A. Kralchevsky, K. D. Danov, and I. B. Ivanov, in *Foams: Theory, Measurements and Application,* edited by R. K. Prud'homme (Elsevier, Amsterdam, 1994), Chap. 1.

[8] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1985).

[9] A. Scheludko and D. Exerowa, Kolloid Z. **165**, 148–151 (1959).

[10] T. T. Traykov, E. D. Manev, and I. B. Ivanov, Int. J. Multiphase Flow **3**, 485–494 (1977).

[11] I. B. Ivanov, Sv. K. Chakarova, and B. I. Dimitrova, Colloids Surfaces **22**, 311–316 (1987).

[12] O. D. Velev, T. D. Gurkov, and R. P. Borwankar, J. Colloid Interface Sci. **159**, 497–501 (1993).

[13] O. D. Velev, T. D. Gurkov, Sv. K. Chakarova, and B. I. Dimitrova, I. B. Ivanov, and R. P. Borwankar, Colloids Surfaces A **83**, 43–55 (1994).

[14] P. Becher, in *Non-ionic Surfactants,* edited by M. J. Schick (Marcel Dekker, New York, 1967), Chap. 15, pp. 478–515.

[15] I. B. Ivanov and D. S. Dimitrov, in *Thin Liquid Films,* edited by I. B. Ivanov (Marcel Dekker, New York, 1988), Chap. 7, pp. 379–496.

[16] E. A. G. Aniansson, S. N. Wall, M. Almgren, H. Hoffmann, I. Kielmann, W. Ulbricht, R. Zana, J. Lang, and C. Tondre, J. Phys. Chem. **80**, 905–922 (1976).

[17] R. J. Hunter, *Foundations of Colloid Science* (Clarendon Press, Oxford, 1987), Vol. 1, pp. 608–611.

[18] S. M. Bailey, S. Chiruvolu, J. N. Israelachvili, and J. A. N. Zasadzinski, Langmuir **6**, 1326–1329 (1990).

[19] P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley–Interscience, London, 1971).