

Spontaneous Cyclic Dimpling in Emulsion Films Due to Surfactant Mass Transfer between the Phases

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A fascinating spontaneous cyclic phenomenon was encountered during observations of aqueous emulsion films between oil phases. Nonionic surfactants (Tweens) initially dissolved in the water phase were used as stabilizers. The films (with typical diameter of 300 μm) were formed in a capillary and were illuminated in reflected monochromatic light. After the films thin down to their equilibrium thickness, a dimple (lens-shaped thicker formation) spontaneously forms and starts to grow around their center. Upon reaching a certain size the dimple forms a channel to the periphery and flows out, leaving a plane-parallel film behind. Immediately afterward a new dimple starts to grow, and so on. This cyclic process could go on for hours. We have proved that the driving force of the process is the surfactant redistribution between the phases. We presume that similar phenomena, resulting from the coupling of the processes of surfactant redistribution and interfacial and hydrodynamic motion inside the films, could be important for the stability of newly formed emulsions. © 1993 Academic Press, Inc.

INTRODUCTION

The stability of the thin interdroplet films in an emulsion system is a major factor determining its resistance against coalescence. Many investigations, both theoretical and experimental, have been devoted to studying the impact of hydrodynamic and direct interactions in such films on their rate of thinning and their stability (See, e.g., Ref. 1). Surprisingly, not much attention has been paid to the stability of thin emulsion films with mass transfer through the interfaces. In a model experimental study of nonequibrated thin films (2, 3), it was found that solute diffusion between the phases considerably changes the film lifetime. It has been shown (4, 5) that most of the observed phenomena are possibly connected with the Marangoni-Gibbs instabilities at the liquid-liquid interfaces (6).

During observation of aqueous emulsion films with surfactant mass transfer toward the surrounding oil phases, we

encountered spontaneous cyclic formation of dimples (lens-shaped thicker formations inside the film). To distinguish between the well known dimpling caused by the hydrodynamic resistance against film thinning (1, 7, 8), we use hereafter the term "diffusion dimpling" in the description of the observed phenomenon. Unlike hydrodynamic dimpling, which occurs only once in the film lifetime, the "diffusion" dimpling phenomenon could go on for many consecutive cycles.

MATERIALS AND METHODS

Xylene (p.a. grade) and water purified by a Milli-Q system (Millipore) were used in the investigations. In one of the experiments the xylene was replaced by commercial refined corn oil. Tween 80 (polyoxyethylene (20) sorbitan monooleate) and Tween 20 (polyoxyethylene (20) sorbitan monolaurate) (ICI Specialties) were used as surfactants.

The model aqueous emulsion films (with a typical diameter of 300 μm) were formed in a meniscus held in a capillary immersed in the oil (9, 10). When the water phase from the meniscus is sucked out, a planar circular film forms in the center. We used a glass capillary with an inner radius of 1.49 mm. The cell assembly is mounted on a metallographical microscope. The evolution of the films is observed through the bottom of the cell by illumination in reflected monochromatic light (wavelength $\lambda = 546 \text{ nm}$). The profile of the film can be reconstructed by registering the pattern of the interference picture (11). A fiber optics and photomultiplier probe allows interferometrical measurement of the film thickness at a given location (12).

Prior to an experiment, the clear aqueous surfactant solution was loaded into the capillary which was afterward carefully immersed in the oil. By varying the pressure inside the capillary, films can be formed and sustained at a certain diameter.

For the sake of comparison, in some experiments the mass transfer between the phases was eliminated by preequilibration of the water and xylene solutions. This was accomplished

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by carefully pouring the oil above the aqueous solution in a wide flask and gently shaking it on a bench shaking machine for more than 24 h.

The distribution coefficients for a certain concentration of both surfactants were determined gravimetrically. Samples of the preequilibrated water and xylene solutions with known weight were carefully dried at 90°C. The remaining surfactant residues were afterward weighed. The water/oil distribution coefficient by weight for an initial aqueous solution of 1.6 wt% of Tween 80 was found to be 9.60 ($\pm 5\%$). The same coefficient for a solution of 0.6 wt% of Tween 20 was 7.25 ($\pm 5\%$).

RESULTS

Description of the Phenomenon

After formation, the films thin down to their equilibrium thickness. Usually during the course of thinning the well known hydrodynamic dimpling (1, 8, 11) is observed. The resulting films are found generally to be thicker than 100 nm due to the electrostatic repulsion between the surfaces (13). As soon as the films reach their equilibrium thickness, a dimple spontaneously forms and starts growing around the center. When the dimple becomes bigger and approaches the contact line, it forms a channel to the periphery and the water inside it flows out, leaving an almost plane-parallel film behind. Just afterward a new dimple starts to grow in the traces of the former one and the process repeats again and again. The cyclic process could go on for hours. The periods between two consecutive oscillations remain approximately constant for many cycles during an experiment and, depending on film diameter and the degree of equilibration, could vary from a couple of minutes to more than 10 min.

An important point to be noted is that, unlike the case of dimples of hydrodynamic origin, during the growth of the "diffusion dimple" the thickness of the surrounding circular plane-parallel film remains almost constant—Fig. 1. Thus, the growth of the thicker formation is sustained by an influx of water from the surrounding meniscus—contrary to the hydrodynamic dimpling, caused by the film drainage.

A schematic representation of the process is drawn in Fig. 2. The typical dimensions of the system and values of the interfacial tension and estimated capillary pressure are enlisted in Fig. 3.

Driving Force and the Role of the Different System Parameters

In order to substantiate that the surfactant diffusion from the water toward the unsaturated xylene phase is responsible for the observed phenomena, we carried out experiments with films formed from preequilibrated phases. No sponta-

neous dimpling was observed in such systems. Similarly, in the case of nonequilibrium initial distribution of surfactant, the formation of dimples stopped after the phases were left inside the cell for more than 24 h. Further, we performed two types of experiments with the equilibrated phases inside the cell:

(i) Replacing the aqueous phase with a new solution (that has not been in contact with xylene). No spontaneous dimpling was observed in this case.

(ii) Replacing the xylene phase with new pure xylene. The intensive spontaneous cyclic process started once again. Thus, the surfactant diffusion out of the film, toward the unsaturated oil phases, appears to be the driving force of the process.

The degree to which the surfactant distribution in the system diverges from equilibrium is obviously the main factor controlling the intensity and the time scale of the spontaneous dimpling. When the oil phase is fully nonequilibrated the process is very intensive; usually after the first diffusion dimple growth and flow out, a channel from the dimple to the film periphery remains open. Through this channel the aqueous phase sucked inside the dimple incessantly drains out. The channel closes in a period of 30 min to more than 1 h, after which the dimple starts oscillating. In order to make the process not so intensive and more smooth, a certain degree of partial preequilibration of the phases is useful. A simple way to accomplish this is to leave the phases in contact for 24 h without shaking. Films formed from such phases oscillate not too intensively, but very regularly. An example of the time scale and repeatability of the process is presented in Fig. 4. The recorded reflected light intensity from a point in the film near the periphery is shown vs real time.

The results of the investigation of the influence of other factors on the behavior of the system are listed hereafter:

Film diameter. Changing the film diameter is the simplest way of controlling the process. The rate of dimple growth is intensified on increasing the area of the film, moreover the cyclic phenomenon manifests itself only above a certain "critical" film diameter. Just below that diameter the spontaneous growth of the dimple would stop at a certain stage, and the formed dimple would remain in a quasi equilibrium position inside the film. At even smaller film diameters no spontaneous dimpling was observed, and the film remained plane-parallel after the outflowing of the hydrodynamic dimple.

Surfactant type and concentration. The "diffusion dimpling" was observed with both Tween 80 and Tween 20 in a wide range of initial surfactant concentrations in the aqueous phase starting from below the CMC up to more than 100 CMC. The intensity and the frequency of the process did not seem to depend appreciably on the bulk surfac-

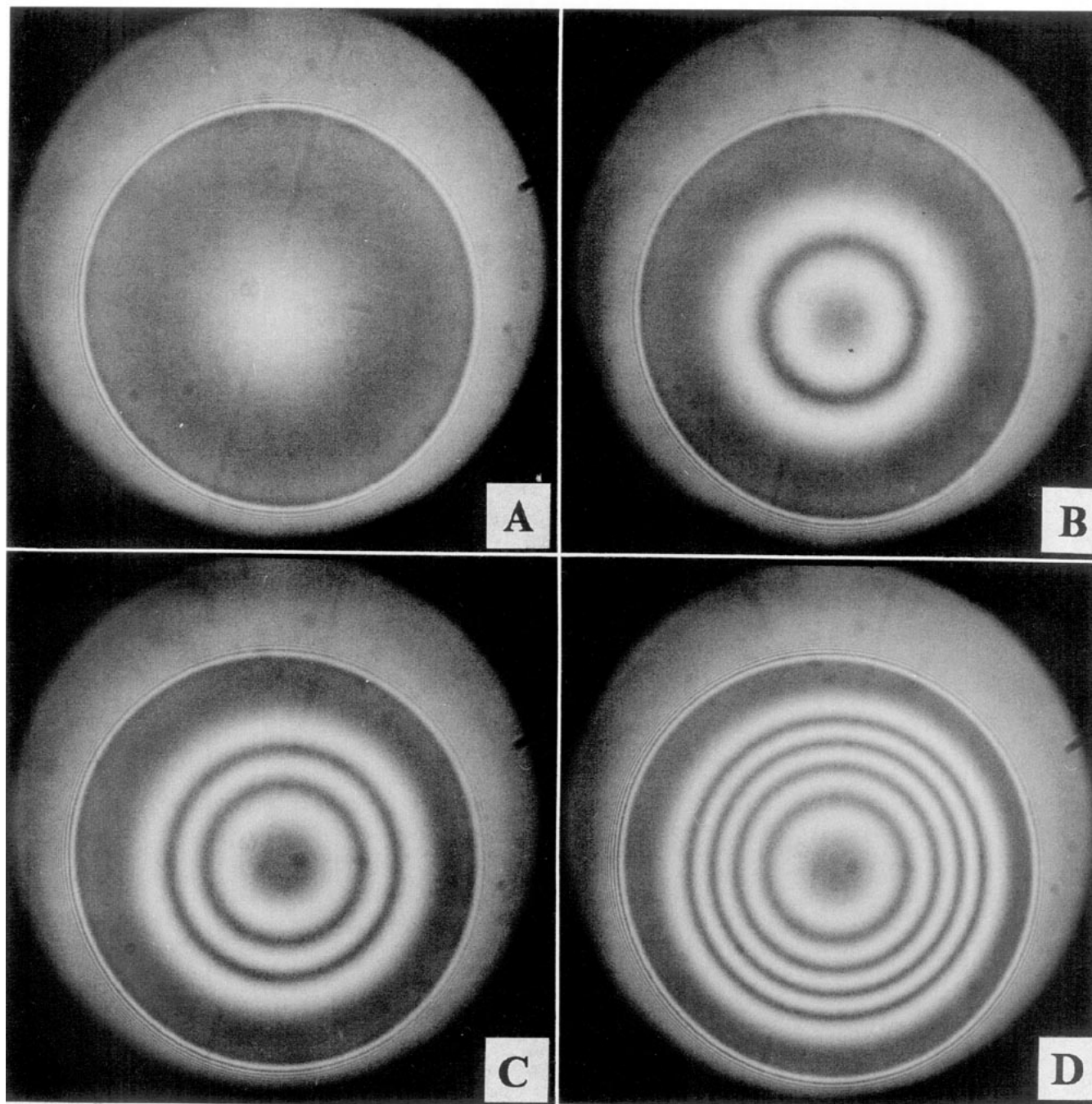


FIG. 1. Four consecutive (A–D) pictures of a spontaneous dimple growth. Note that the thickness at the circular plane-parallel portion of the film between the dimple and the meniscus remains approximately constant (no change in the reflected light intensity). Film diameter, $330\ \mu\text{m}$.

tant concentration. For example, films with a diameter of $420\ \mu\text{m}$ formed from partially preequilibrated (see above) Tween 80 solutions had a mean cycle period of 18 min for 10 CMC solution and 15 min for 1000 CMC solution. Having in mind that the interfacial adsorption Γ does not change appreciably after CMC, the above observation may imply

that the phenomenon depends on the interfacial rather than on the bulk properties of the surfactants.

Electrolyte concentration. Addition of electrolyte (NaCl) decreases the films ability to form “diffusion dimples.” Due to the suppressed electrostatic repulsion the films thin down in spite of the surfactant depletion tending to suck liquid

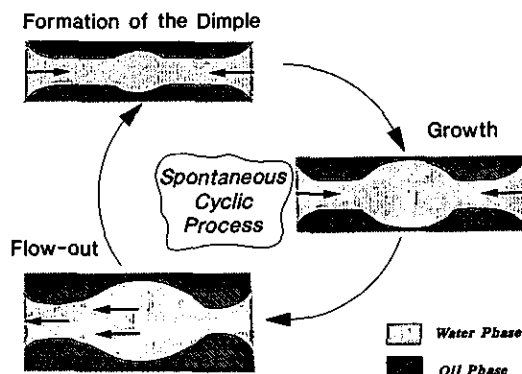


FIG. 2. A schematic presentation of the main stages of the spontaneous cyclic process (cross section perpendicular to the film surfaces; film and dimple dimensions not in scale).

inside. In the case of films stabilized with Tween 80 the spontaneous dimpling seemed to be completely blocked at electrolyte concentrations higher than $5 \times 10^{-3} M$. Only hydrodynamic dimpling was observed at such concentrations and the films ruptured at a certain stage of thinning (at a thickness below 100 nm).

Oil phase. Besides xylene, corn oil was also used in one of the experiments and the "diffusion dimpling" was registered with that oil phase too.

DISCUSSION

The described behavior allows us to suggest that the growth of the dimple originates from the depletion of the surfactant in the film—both from the interfaces and from the film interior (see Figs. 5A and 5B). This depletion is a result of its retarded diffusion from within the aqueous meniscus toward the film center. No similar reasons for decreased diffusion are expected to exist from the oil side of the film interfaces. Following the depletion, tangential movement of the surfaces (connected with the Marangoni effect, Fig. 5C, see also Refs. 4, 5, and 6) appears. The movement is coupled with con-

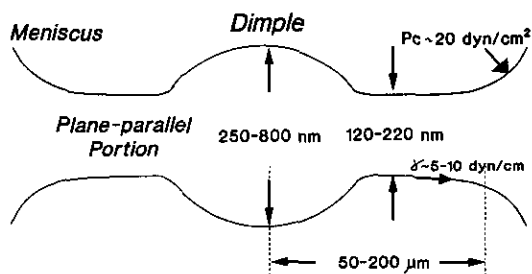


FIG. 3. Typical dimensions of the film and values of other parameters at which the "diffusion dimple" phenomenon was observed.

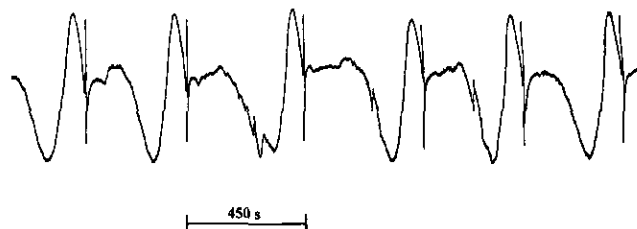


FIG. 4. Experimental data on the reflected light intensity vs time for a film with spontaneous cyclic dimpling. The film diameter is $225 \mu m$. The surfactant is Tween 80 at 100 CMC (partially preequilibrated phases). The intensity is scanned at a point near the periphery. With the increase of the film thickness at first it goes down, and then up. Each outflow of a dimple is recorded as a sharp vertical line.

vective fluxes inside the film, feeding the dimple—Fig. 5D. The growth of the dimple goes on until it reaches the film meniscus, and afterward a swift outflow and return to the initial plane-parallel film follows.

The diffusion dimpling seems to be a process leading to stabilization of the thin emulsion films by sucking additional aqueous phase between the droplets. *One may expect the factors of stabilization connected with this phenomenon to also be active during the interaction of newly formed emulsion drops without dimpling in the film between them and even if there is no interdroplet film at all (with the single prerequisite that the surfactant is dissolved initially only in the continuous phase).*

When an emulsion is formed in industry, usually the surfactant is initially dissolved into one of the phases. The homogenization process then is accomplished in a few minutes or less. Right after the fragmentation of the drops, intensive coalescence may take place before stable, compact emulsifier layers have adsorbed at the drop interfaces. Sources of sta-

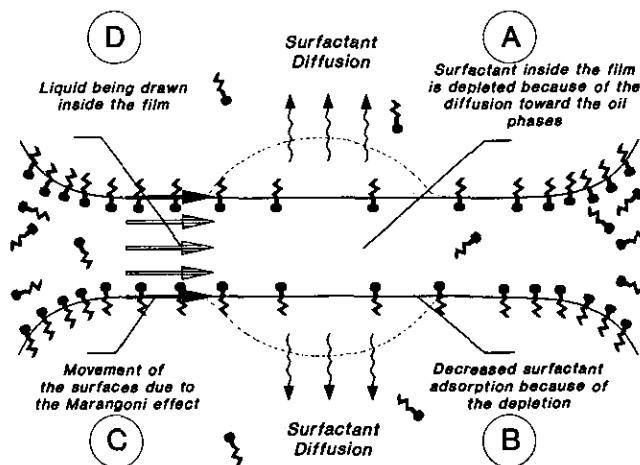


FIG. 5. A schematic presentation of the factors (A–D) leading to the "sucking in" of liquid inside the film and formation of the "diffusion" dimple.

bilization arising from surfactant redistribution between the phases could be operative and important for the behavior of the emulsion for a certain time after the homogenization process.

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