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Investigation of Thin Liquid Films of Small Diameters and High Capillary Pressures by a Miniaturized Cell

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A highly miniaturized cell for the experimental investigation of thin foam and emulsion films has been constructed. The miniaturization of the structure in the new design is achieved by forming the cell out of thin glass slides drilled by excimer laser and sintered into a single structure. The capillary pressures and film dimensions attainable in our type of cell are closer to reality than those in the currently deployed models. Parallel experiments on the formation and thinning of emulsion films stabilized with nonionic surfactant (Tween 20) and with protein (BSA) have been carried out in the newly designed and in the conventional cell. The data reported in the paper show that the patterns and the time scales of film evolution in the two cells are significantly different. No dimple formation in the realistic films has been observed. A particularly drastic difference in the time scales is recorded in the case of protein-stabilized systems, probably resulting from the increased interfacial viscosity and elasticity. © 1995 Academic Press, Inc.

Key Words: thin liquid films; capillary pressure; dimple; nonionic surfactants; protein-stabilized emulsions.

INTRODUCTION

In any foam or emulsion system thin liquid films are formed when the droplets or bubbles are pressed against one another under the action of surface forces, Brownian motion, or gravity. The thinning pattern and the stability of these thin films against rupture are the main factors controlling the overall emulsion or foam lifetime and behavior. Many researchers have aimed to investigate in a controllable and reproducible way the formation, dynamics, and thickness of such thin films. Derjaguin has pioneered the use of experimental cells for creating and interferometrically observing thin foam films (1, 2). The principles of film formation and observation implemented in Derjaguin's prototype were later used in the improved cell designs described below. A more detailed overview of the early attempts in this field can be found in the monographs of Scheludko (3) and Sonntag and Strenge (4).

Currently, emulsion films are usually investigated by microinterferometric techniques in a type of cell originally proposed by Scheludko and Exerowa (3, 5, 6; called further, for simplicity, "conventional" cell). While its principle of operation is similar to that of the cell of Derjaguin, this cell is easier to produce, align, and handle and over the years has been proven to be a valuable and effective tool for studying the behavior and the intermolecular interactions of thin liquid films (6). A schematic diagram of this cell is presented in Fig. 1. The film is formed by sucking out liquid from a biconcave meniscus inside a capillary of inner diameter 2–4 mm.

Theoretical research on the rate of thinning of foam and emulsion films both in the presence and in the absence of surfactants has been widely reported (7–9). Most of the derived formulas modify the well-known Reynolds equation (9, 10) for the velocity of thinning V_{Re} of a film between tangentially immobile solid surfaces, which in terms of driving pressure reads

$$V_{Re} = \frac{2h^3\Delta P}{3\mu R^2}, \qquad [1]$$

where h is the film thickness, ΔP is the driving pressure, equal in our case to the capillary pressure inside the cell or in the drops, μ is the viscosity of the film phase, and R is the film radius. Though the rate of film thinning in emulsion systems may exceed the Reynolds rate by some orders of magnitude, the functional dependence on ΔP and R is preserved so long as surfactants are present (7, 9). Therefore, in any emulsion system the driving (capillary) pressure and the film radius are two parameters that crucially affect the rate of thinning of the interdroplet films and, consequently, the stability of the system.

From this theoretical viewpoint, the conventional cell has two principal shortcomings in the modeling of film thinning dynamics:

(i) The typical diameters of the observed films (above 100 μm) are much larger than those encountered in real

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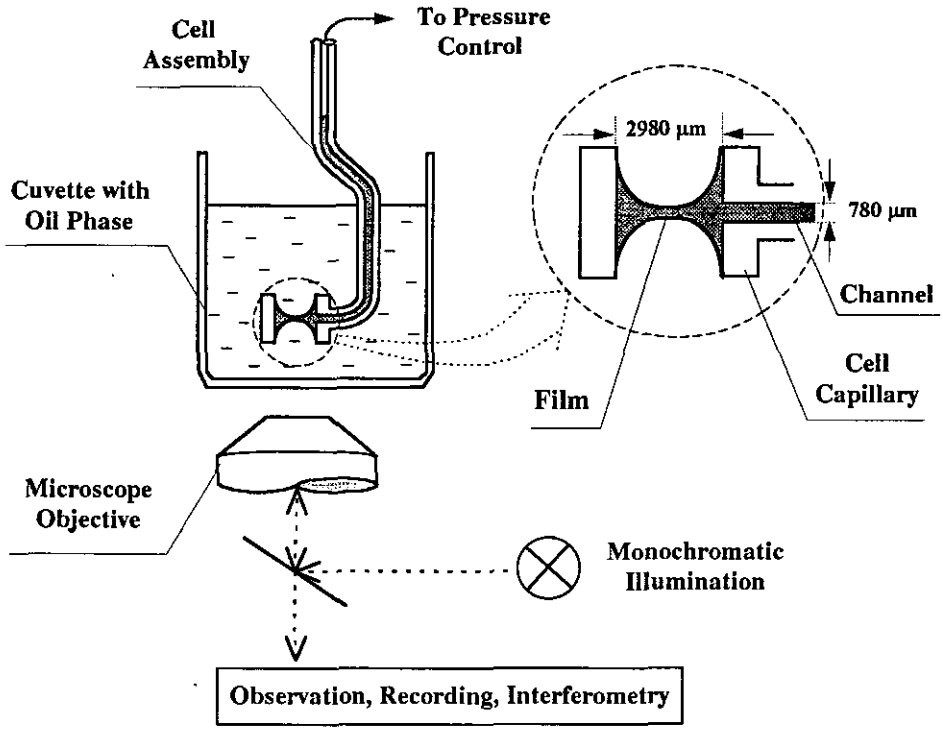


FIG. 1. Schematic diagram of the conventional cell for investigation of thin liquid emulsion films. The films are formed in the cell capillary by sucking through the side channel. They are observed in reflected monochromatic illumination.

systems. This causes dimpling and other effects that (as it turns out) may be absent in practical batch emulsions.

(ii) The capillary pressure inside the films (that is, the driving pressure of film thinning according to the theory) is much smaller than that in real emulsion systems. The capillary pressure is an important parameter which determines not only the rate of film thinning but also the equilibrium film thickness.

The second shortcoming is avoided using the porous plate cell proposed by Mysels *et al.* (11–13). This cell allows the attainment of very high capillary pressures (up to 10^6 dyn/cm^2). However, the diameters of the films inside it are larger than those in the Scheludko cell, which takes them even further away from the real systems. Moreover, the film contact angle, which is an important parameter characterizing the interactions between the film surfaces, cannot be observed in the course of the experiments.

We have constructed a miniaturized cell of new design by the use of etched-and-fused structures in glass plates. Our cell allows the study of films that are smaller and subjected to an order of magnitude higher capillary pressures than those in the conventional cells. The construction of the cell is described in the following section. Emulsion films containing nonionic surfactants or proteins were investigated using the newly constructed cell, and a comparison with the thinning patterns of films in conventional cells is reported under Results. An overview of the characteristic parameters of the films formed in our cell, compared with those in the Scheludko and Mysels cells and with real emulsion systems, is given under Discussion.

CONSTRUCTION OF THE CELL

The principle of operation of the cell is close to that of the conventional type, but thanks to its new design the dimensions of the capillary into which the films are formed, as well as of the side opening, have been decreased about 10-fold. These dimensions determine the capillary pressure and the diameters of the films formed inside the cell (see below). The miniaturization of the structure allows the attainment of parameter values that are closer to those of real batch emulsion systems. The whole assembly is sintered (fused by heating) so that a structure of microscopic channels and orifices is formed inside a glass plate of thickness below 0.36 mm. A schematic diagram of the cell is presented in Fig. 2.

The basic structure was prepared from a couple of microscope slides (Chance Propper Ltd., 24 × 50/0.17 mm). Using an excimer laser driven by micromachinery, vertical holes (diameter ≈280 μm) designed to serve as capillary tubes were drilled through both plates; further, one hole was drilled through the upper plate to serve as an outlet opening. The holes were connected with a horizontal channel (with cross-sectional dimensions of 90 × 50 μm) formed in the upper plate. Afterward the plates were sintered together by carefully aligning them on top of one another and heating

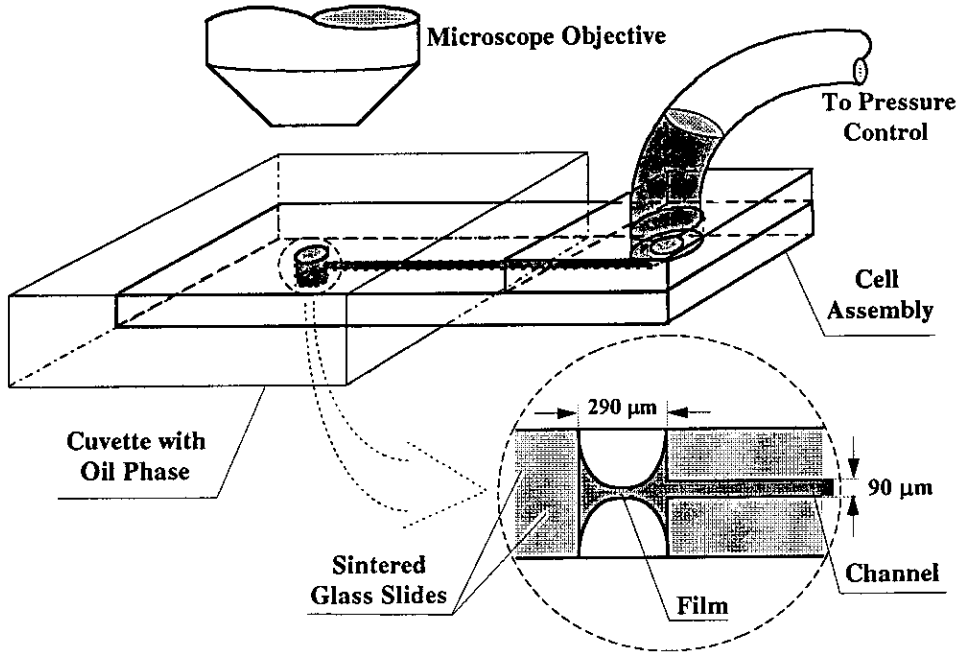


FIG. 2. Schematic diagram of the newly designed cell for investigation of thin liquid films. The films are formed into the opening of the sintered pair of glass slides. The cell assembly is immersed into the disperse (oil) phase poured inside the cuvette.

them inside a programmable furnace (Heraeus, Termicon P) gradually up to 670°C for 20 min. In order to create an outlet port suitable for attaching a tube of Teflon or polyethylene, a thicker (2 mm) glass plate with a hole of appropriate diameter was sintered above the outlet opening of the upper microscope slide. The slow cooling of the sintered plates in a period of about 24 h was of crucial importance for the quality of the whole assembly, as cracks inside the structure are apt to appear at higher cooling rates.

Under working conditions the cell was inserted into a thin cuvette with optically clear walls, which held the disperse (oil) emulsion phase. The cell and the cuvette were mounted on a special metal stand, which could be fixed on the table of the reflected illumination microscope (Jenavert from Carl Zeiss, Jena). The microscope together with the cell was inclined by approximately 40° to ensure that the outer liquid stayed inside the cuvette. The observations were carried out by using a long-focus objective (Zeiss PA-LD 25×/0.50).

As the construction of the cell included only glass and PTFE tubing in contact with the investigated phases, it could be thoroughly cleaned by chromic acid before the experiments. The small volume of the cuvette allowed quick and easy thermostating during the experiments.

RESULTS

In order to compare the dynamics of the film thinning in the newly designed cell and in the Scheludko and Exerowa cell, we carried out parallel experiments on the formation of emulsion films in both these cells. Compared to our newly produced cell with an opening of 280 μm, the inner diameter of the used conventional cell (described in Ref. 14) was 2980 μm. The aqueous film phase contained either the nonionic surfactant Tween 20 (polyoxyethylene 20 sorbitan monolaurate) or the protein BSA (bovine serum albumin). The surfactant was supplied by ICI Specialities. BSA of low fatty acid content was obtained from Sigma, Cat. No. A-7511. The electrolyte concentration was adjusted with the use of NaCl, a Merck product additionally baked for 4 h at 450°C. Xylene (p.a. grade) was used as the disperse phase.

It was established earlier (6, 14, 15) that the thinning behavior and the final thickness of emulsion films containing polyoxyethylene chain nonionic surfactants are strongly influenced by the presence of electrolyte, as electrostatic repulsion is present between the surfaces. Therefore, the experiments with Tween 20 were carried out with two aqueous phase solutions of different electrolyte (NaCl) concentration, namely 5×10^{-4} M in the first solution and 10^{-1} M in the second. Both solutions contained Tween 20 at a concentration of 3×10^{-3} M. This concentration is about 60 times the CMC (16) and based on earlier studies (14), we expected to obtain stable films with clearly defined thinning pattern. In order to avoid mass-transfer effects, which were previously reported to be important for the behavior and stability of thin emulsion films (17), the phases were preequilibrated by the procedure described in Ref. (14).

The BSA solution contained 0.05% wt. protein at an electrolyte concentration of 10^{-3} M. The pH of the prepared solution was not specially adjusted, but prior to the experiments was measured to be 5.5 ± 0.05. To avoid the possibility of protein aggregates, dust, and bacteria getting in the studied films, the protein solution was filtered through a

0.22-μm-cutoff filter (Millex-GV, Millipore) before being loaded into the investigation cells.

The oil/water interfacial tension for the investigated systems was measured with a de Nouy ring tensiometer following the procedure described earlier (18). The interfacial tension between xylene and water in the system with Tween 20 was 3.8 $\pm$ 0.1 mN/m and in the protein system was 14.5 $\pm$ 0.2 mN/m.

In all experiments the films were formed by a gradual decrease in the pressure in the aqueous phase during a period of 5 to 10 s. The diameters of the films in the conventional cell were sustained at 250 $\pm$ 20 μm. Data for at least 10 films were video-recorded in each case and processed. Videotaped images were digitized on PC-compatible computer equipped with a TARGA+ 16/32 board. Typical patterns of film thinning are shown in Figs. 3, 4 (Tween), and 5 (BSA).

All of the phases of film thinning reported in the literature (9) were observed when films containing Tween 20 were formed in the conventional cell. A thick lens-like formation called dimple (9, 19) appears between the film interfaces during the first stages of the process (Figs. 3e and 4e). The dimple later merges with the liquid in the meniscus at a point at the film periphery (Figs. 3f and 4f). After the dimple flows out, the films thin down as plane-parallel ones, although they usually incorporate some remaining part of the dimple (Fig. 3g). At high electrolyte concentration, a transition to a "secondary" black film (11, 20, 21) is observed below a certain thickness (Fig. 4g). The thinning process ends with a primary (Fig. 3h) or a secondary (Fig. 4h) film of uniform and equilibrium thickness, which may also incorporate some thicker lenses. This last stage is reproducibly reached in a period of about 180 s.

In contrast, during the thinning process in our new cell we were not able to observe film thinning at constant diameter. This happens because the films reach their lowest thickness after a period shorter than 5 s, which is comparable with the time of their formation by suction in the cell (Figs. 3b and 4b). After the lowest equilibrium thickness is reached, the films increase in diameter without any substantial change of this thickness (Figs. 3c, 3d and 4c, 4d). Thus, the thinning pattern in the miniaturized cell includes a very swift ($\approx$2–3 s) formation of a film of equilibrium thickness smaller than 50 μm in diameter, which later spreads to a larger area. This mechanism is essentially different from that in the conventional cell.

A certain similarity in the patterns of film thinning inside the new and the conventional cell can be found only at the high electrolyte concentration after the transition to a black film, since in both cases part of the liquid remains entrapped in the film (Figs. 4c and 4g). This liquid forms lenses later (Figs. 4d and 4h), which disappear in a period longer than 60 s.

The results from the investigations with BSA-stabilized films are presented in Fig. 5. The thinning patterns in the new and the conventional cells are similar to those in Fig. 3, but the time scales of the processes are even more divergent. While the dimpleless film in the new cell is formed by spreading in a little over 10 s (Figs. 5a–5d), the large dimple formed in the conventional cell disappears in a period exceeding 600 s. There also exists a difference in the stability of the films in the new and in the conventional cell. The films in the new cell rupture immediately after their formation (for the film presented in Figs. 5a–5d the rupture occurs at 11.7 s). In contrast, the films in the conventional cell always stay intact for periods exceeding 15 min.

One interesting detail that can be noticed in Figs. 5b–5d sheds light on the mechanism of film formation by "spreading," observed with the new cell. A small particle, probably comprising aggregated protein, has been entrapped between the film surfaces (Fig. 5b; position of particle marked with arrow). This particle does not change its position with respect to the film center during the further evolution of the film (Figs. 5c–5d). Therefore, at least in the case of BSA, the film evolution by spreading in the new cell seems to occur under the conditions of full tangential immobility of the film surfaces.

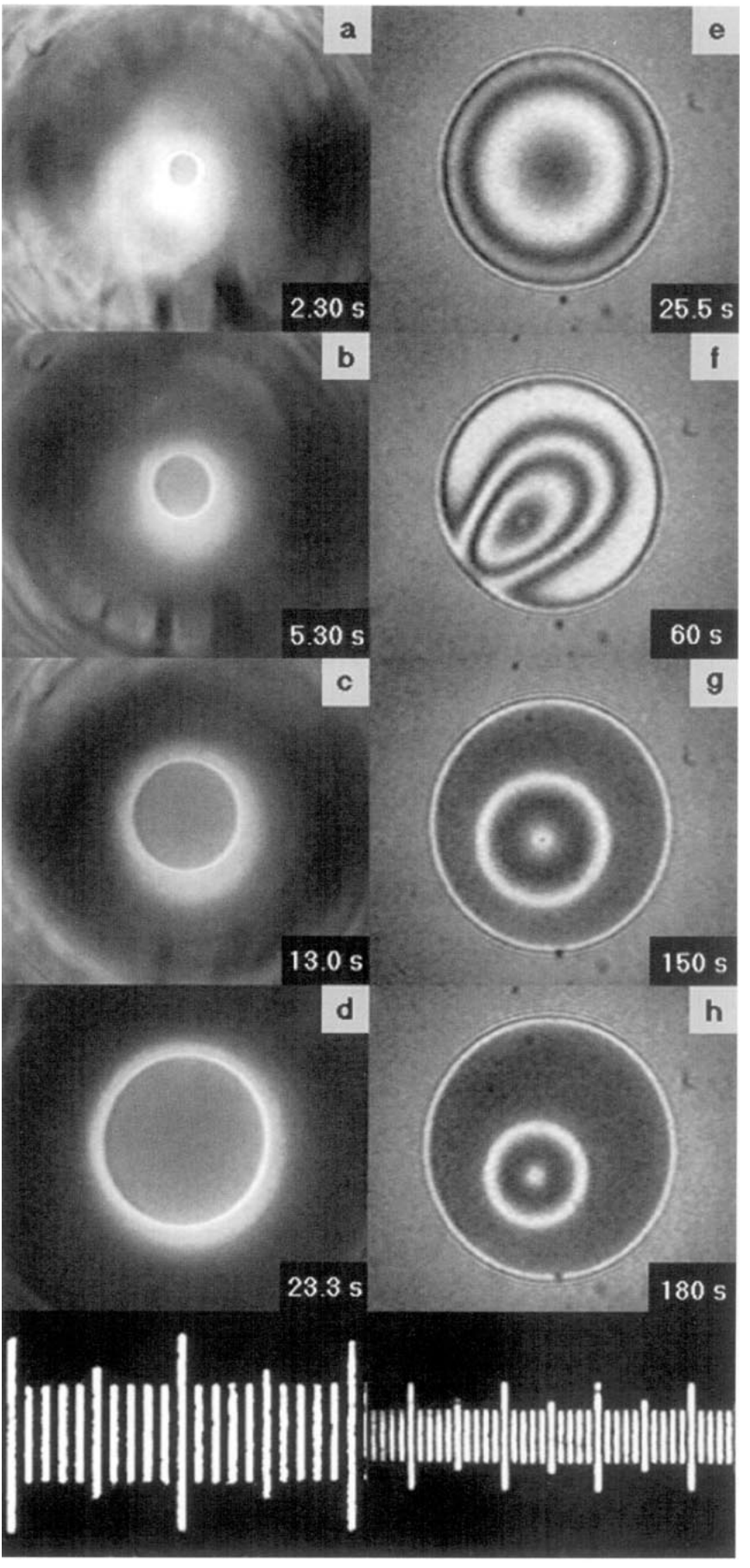
In summary, it has been proven that the newly designed cell is capable of producing foam or emulsion films ranging from 20 to 220 μm in diameter. The process of thinning of these small films is faster by about one order of magnitude than that in the conventional cells and follows a totally different mechanism. The small films are spread out by increasing their diameter without forming a dimple.

DISCUSSION

On the basis of the available data for our miniaturized cell and the known characteristics of the Scheludko and Exerowa and Mysels cells, we have estimated the range of capillary pressures vs film diameters that are attainable in the three types of cells. The range of capillary pressures was calculated based on the formula proposed by Toshev and Ivanov (22),

$$\Delta P = \frac{2\gamma R_c}{R_c^2 - R^2 \cos\theta},$$

where R denotes the film radius, R_c the radius of the cell capillary, γ the interfacial tension, and θ the contact angle between the film and the meniscus. In the calculations we have assumed that both θ and the contact angle between the liquid of the film and the capillary are close to zero. The estimated regions of the attainable parameters for the three types of cells are plotted in Fig. 6. The interfacial tension has been varied in the widest possible range of 1–20 dyn/cm, thus outlining the region of possibly accessible parameters. The limiting, highest capillary pressure that could be obtained in a given type of cell is determined by the diameter of the side channel through which the liquid inside the me-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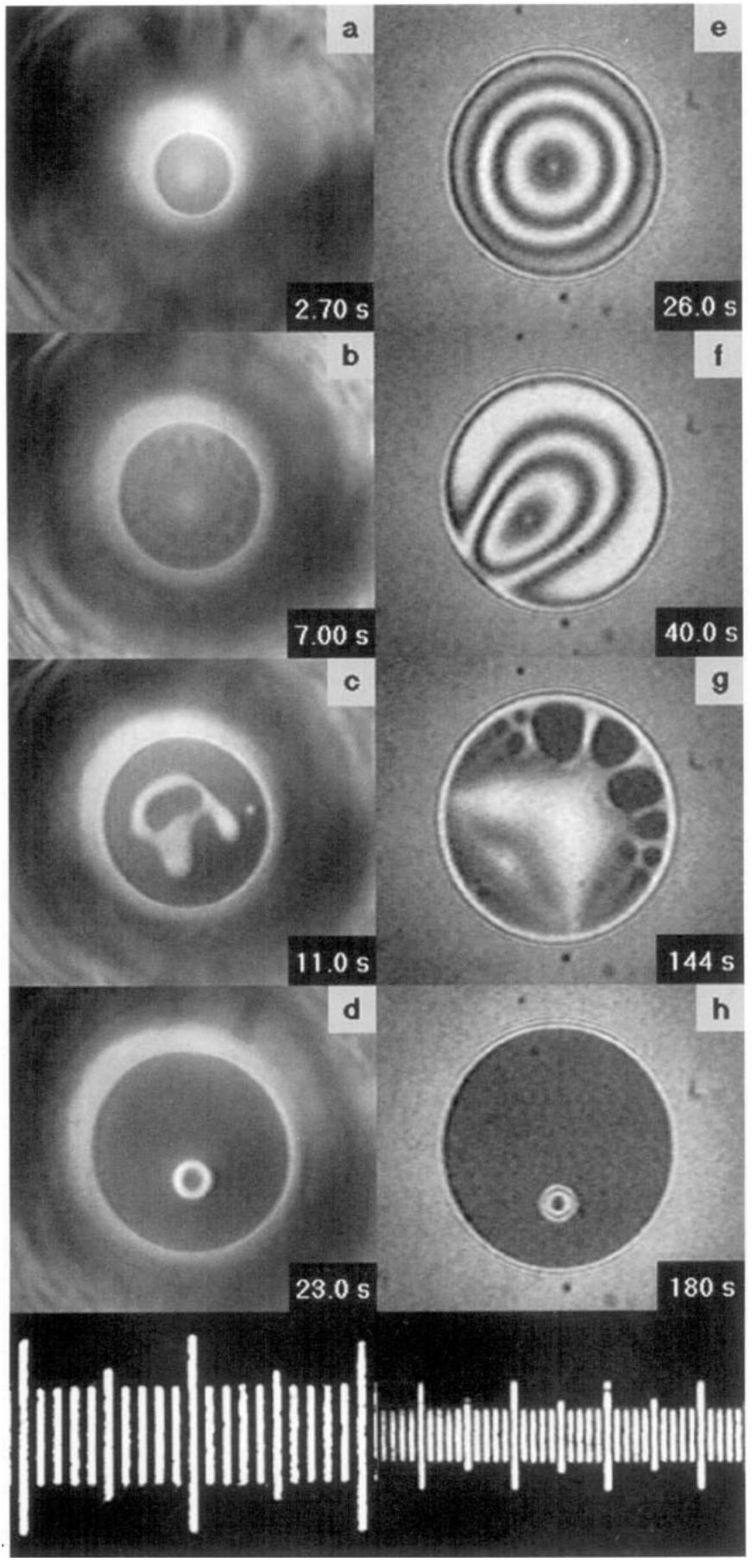
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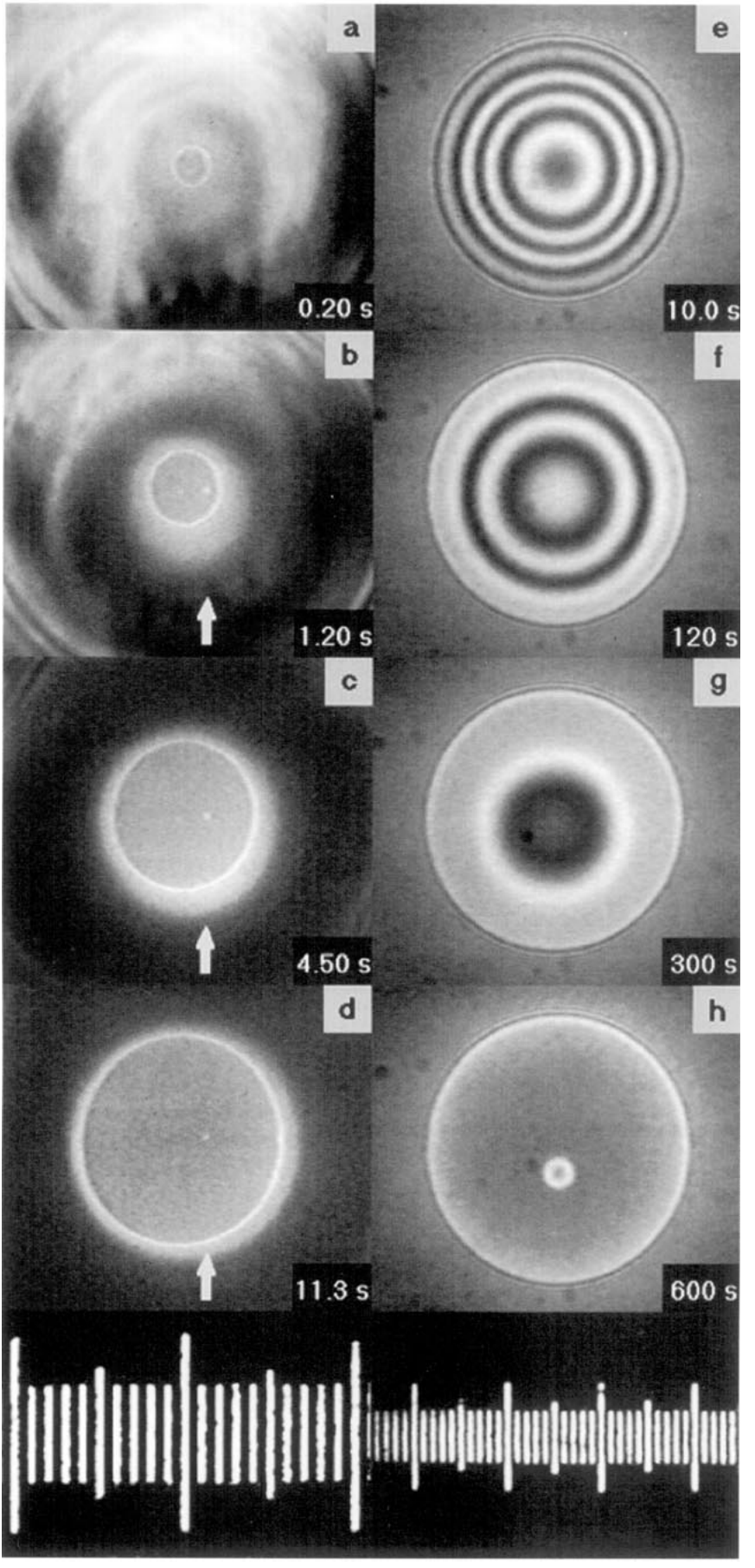
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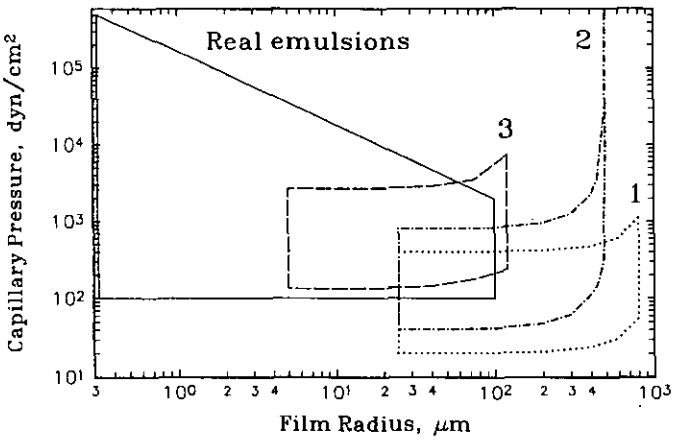

FIG. 6. Comparison of the film radii vs capillary pressures attainable by the different types of experimental cells: (1) Conventional (Scheludko and Exerowa) cell; (2) Mysels porous plate cell; (3) new miniaturized cell.

niscus is sucked out. Due to the decreased dimensions, the limiting pressure in our newly designed cell is about an order of magnitude higher than that in a typical conventional cell. The limiting pressure in the Mysels type of cell is dependent on the pore size distribution of the glass plate. When plates with very small pores are used, the limiting pressure could reach up to 10^6 dyn/cm^2 (6, 11), though in this case the film diameter remains virtually constant and equal to the diameter of the cell opening (hence the high, narrow peak in Fig. 6, plot 2).

In Fig. 6 we also compare the attainable pressure/film size values in the three types of cells with the range of corresponding parameters for practical batch emulsion systems. It is known that when emulsion droplets are pressed against each other to form a film inbetween, the driving pressure of film thinning (ΔP in Eq. [1]) is equal to the capillary pressure inside the droplets P_c (9, 23). The latter is connected with the droplet radius, r_d, through the well-known Laplace equation

$$P_c = \frac{2\gamma}{r_d}.$$

The plot for emulsions in Fig. 6 is made assuming that the emulsion droplet radii r_d could vary between 1 and 250 μm. The radii of the films between the droplets in a real emulsion depend on the forces bringing the droplets together. In Fig. 6 we span the range from 0 up to $r_d/3$ (last value being close to packing of deformed droplets in a highly compressed creamed layer).

Figure 6 demonstrates that while the Scheludko and Mysels cells could cover only very limited areas of the real emulsion parameters, our cell goes out much further into the range of real systems. It can also be used to study phenomena of theoretical and practical importance that are sensitive to both film size and capillary pressure. Such phenomena include the stratification (layer by layer thinning of thin liquid films) (24) mass-transfer effects ("diffusion dimpling") (17) and coalescence of ganglia in porous media during enhanced oil recovery (25). In addition to more realistic capillary pressures and smaller film dimensions, the new cell possesses some purely experimental advantages, namely, the use of very small quantities of liquid and easy temperature control. On the other hand, measuring the thickness and contact angles of equilibrium films in the conventional cell seems to be easier and more precise.

The observed very fast thinning of small films in the miniaturized cell (Figs. 3–5) is in full accord with the theoretical expectations outlined in the Introduction. Therefore, the time of the interdroplet film drainage in real emulsion systems seems to be restricted to less than a few seconds. No dimpling could be expected in these interdroplet films. Moreover, our data (Figs. 3–5) suggest that, instead of the currently adopted model (film formation and thinning down to equilibrium thickness), the real hydrodynamic interdroplet interactions in emulsions could follow a different pattern, including the formation of small films of equilibrium thickness and their expansion. This behavior could be explained by the theory of so-called inverse thickness (thickness of film formation) (9). Theoretical study in this direction is under way.

The parallel experiments, presented in Figs. 3–5, demonstrate also the impact of the interfacial elasticity and viscosity on the thinning pattern of liquid films. When the surfaces are highly viscous and rigid (as in the case of protein), a large and very slowly disappearing dimple is formed with the conventional cell. This dimple formation is avoided in the newly developed cell, and the differences between the time scales of the two processes become even more pronounced. Recent theoretical developments (26) have shown that the interfacial viscoelasticity is an important parameter decreasing the rate of thinning of films between small drop-

FIG. 3. Digitized images of the emulsion film evolution in the new (a–d) and in the conventional (e–h) cells. The continuous aqueous phase contains Tween 20 and 5×10^{-4} M electrolyte. The film in the miniaturized cell is plane-parallel and does not change its thickness after stage (b). The film in the conventional cell comprises a big dimple which slowly decreases. The scales of the film dimensions are presented in the lowest two frames; 1 div = 10 μm.

FIG. 4. Same as Fig. 3, but the aqueous phase contains 0.1 M electrolyte. In this case a transition to a very thin ("black") film is observed with both types of cells (frames b and g).

FIG. 5. Digitized images of the emulsion film evolution in the new (a–d) and the conventional (e–h) cells, when the aqueous phase contains BSA. The difference in the timescales of the processes is particularly drastic in this case (compare with Fig. 3). The arrows in frames (b–d) point to a small particle which demonstrates the tangential immobility of the film surfaces.

lets and bubbles. In the case of small films the energy dissipation in the film region is comparable with that in the surrounding meniscus. In contrast, the dissipation of energy in the thinning films between large droplets or bubbles occurs exclusively in the thin film itself. The above theoretical conclusion is in qualitative agreement with the thinning patterns presented above in Figs. 3–5.

From a practical viewpoint it is known that the formation of a dimple in the conventional cells can provoke serious experimental difficulties when protein is used as a stabilizer. This happens because the dimple may become encapsulated (27), or the time of drainage of the films may be very prolonged. The "spreading" mechanism of film formation in the newly designed cell allows us to avoid this problem.

CONCLUSIONS

The experimental comparison of the time scale and the pattern of thinning of emulsion films stabilized with the nonionic surfactant Tween 20 has revealed that the films in the newly designed miniature cell thin down an order of magnitude faster than those in the conventional cell. The difference in the time scales of film formation and thinning is even larger when the films are stabilized with protein (BSA). Most important, the pattern of thinning in the miniaturized cell is significantly different, as it does not include dimple formation and the films spread to their final diameter rather than thin to it as observed previously. This new thinning pattern is probably close to that occurring in the interdroplet films in real batch emulsions.

On the basis of the experience achieved, we expect that the new construction of the cell could be advantageous in the following areas of colloid research:

(i) The hydrodynamic evolution of realistic (small in size and subjected to high capillary pressures) emulsion films can be studied. As far as we know, this field has not yet been explored experimentally.

(ii) Some phenomena in foam and emulsion films like stratification (24), mass-transfer effects (17), and ganglion coalescence (25) can be studied in the new cell at simultaneous values of film size and capillary pressures not attainable by the conventional methods.

(iii) As the films in the new cell are formed by spreading rather than thinning, the new cell may be applicable to the study of films with high interfacial viscosity (like these stabilized with proteins) where the dimpling in the conventional cells presents serious experimental handicaps.

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