

# A bike-wheel microcell for measurement of thin-film forces

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## Abstract

A thin-film balance employing either a Sheludko capillary or a Mysels-inspired porous-medium film holder provides a direct measurement of disjoining-pressure isotherms in free, liquid thin films. However, each film holder suffers its own distinct disadvantages spanning non-uniform and slow liquid exchange, a limited range of measurable disjoining pressures, an inability for reuse, and a requirement for significant chemical amounts. In an attempt to alleviate these disadvantages, we have designed and constructed a miniaturized and microfabricated ‘bike-wheel’ cell as a replacement film holder. Essentially, an inner hole holding the thin film (the hub) is connected radially by 24 small channels (the spokes) to an outer, larger size annulus (the wheel). This design provides a hybrid of the Sheludko capillary and the Exerowa–Sheludko porous-plate film holders and eliminates the undesirable features of each. Moreover, due to its miniaturized dimensions and concomitant fast drainage rates, the bike-wheel film holder is particularly suited for investigation of polymer and/or protein-based systems where thin-film force laws depend on the degree of aging at the interface. The new bike-wheel microcell is validated quantitatively by reproducing a known disjoining-pressure isotherm for 0.1 M aqueous sodium dodecyl sulfate (SDS) foam films, including dynamic stratification, and reversible and oscillatory isotherm branches. Finally, application of the new bike-wheel film holder is made to thin-film forces in aqueous protein-stabilized foam films of bovine serum albumin (BSA) at the isoelectric point. Here we find a repulsive, steric stabilized disjoining-pressure isotherm for fresh protein films, but surface aggregation and non-equilibrium forces for aged films. The new bike-wheel microcell incorporated into the thin-film balance provides a useful tool for studying thin-film forces, especially for larger molecular weight stabilizing species. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Bike-wheel microcell; Thin-film forces; Disjoining-pressure isotherms

## 1. Introduction

Knowledge of the colloidal forces in single, free-liquid films, i.e. the disjoining-pressure isotherm, is critically important to understanding

and controlling the behavior of foams, emulsions, and pseudoemulsions. Direct measurement of the disjoining-pressure isotherm for an aqueous surfactant film surrounded by air was apparently first undertaken by Sheludko and Exerowa in 1959 [1]. The technique involved forming a liquid film in a small glass capillary and subjecting that film to a known capillary pressure,  $P_C$ , which is the difference between the bulk gas and bulk liquid pressures. Film thickness was measured by

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microinterferometry [2]. At equilibrium, the imposed capillary pressure equals the disjoining pressure; thus, by varying the capillary pressure, i.e. by varying the gas pressure relative to the liquid pressure, the disjoining-pressure isotherm is traced out. This device is now known as the thin-film balance [3,4], and the capillary in which the liquid film resides is commonly referred to as a Sheludko cell.

Two disadvantages of the Sheludko cell relate to the small hole that connects the film to the surrounding bulk liquid. First, when the applied capillary pressure exceeds the capillary entry pressure of the connecting hole, then force measurements are no longer possible. Second, the single connecting hole results in unequal drainage around the perimeter of the film. To overcome these difficulties Mysels [5] suggested in 1964 and later Mysels and Jones [6] used a liquid-wetting porous glass ring sealed into a Perspex holder in place of the glass capillary of Sheludko. In this manner, both higher disjoining pressures are accessed (up to the non-wetting-phase entry capillary pressure of the porous medium) and more uniform drainage is possible.

Soon after the invention of the Mysels' cell, Exerowa and Sheludko [7] proposed an improved porous-plate film holder. Here to form the liquid film, a small hole is drilled through a porous-glass or porous-ceramic plate with the bulk liquid connected to the porous medium via a glass capillary. The porous-plate cell of Exerowa and Sheludko inserted in the thin-film balance is currently the most popular apparatus to measure thin-film forces in free-liquid films [3,4].

Unfortunately, there are also disadvantages to the porous-plate cell. Because the porous medium exhibits high surface areas in contact with the liquid solution, adsorption and plugging may occur when studying larger molecular weight species, such as polymers and proteins. Also, the resulting contamination of the porous medium demands a new film holder for each new solute type and concentration studied. Although rather high disjoining pressures can be reached, radial drainage from the film in the porous plate is only approximated. Finally, in the cases where significant amounts of protein, polymer, or specialty

surfactants adsorb on the internal surface of the porous plate, large amounts of sample are necessary to saturate all pores in the porous medium. Typically, only small quantities of these species are available for investigation; in this sense the porous-plate holder is somewhat limiting.

To overcome these difficulties we have implemented a new miniaturized 'bike-wheel' cell for use in the thin-film balance. Our design takes advantage of the low surface area and reusability of the Sheludko cell while also incorporating uniform radial drainage and high capillary pressures of the porous-plate cell. We construct a hybrid of the two cell types using now standard microfabrication techniques. Basically, a central hole holding the liquid film is connected by a series of very small channels, emanating radially outward to a circumscribing annular channel (hence the coinage of a bike-wheel). This outer annular channel is then connected through a single channel of the same dimensions to a standard glass capillary tube for mounting in the thin-film balance. The shallow spoke channels are responsible for the high entry capillary pressures; thus, a wide range of disjoining pressures is attainable, comparable to that obtained with the porous-plate cell. The annular channel of the bike-wheel cell is of wider dimensions to ensure little resistance to flow and fast drainage.

The bike-wheel cell is similar to the recent cell of Velev et al. [8] in that it is microfabricated. However, the design of Velev et al. is essentially a scaled-down Sheludko capillary cell. Our experience with this cell is that somewhat uneven and extremely low drainage rates arise. We overcome these difficulties with the new bike-wheel pattern. This paper describes the design and construction of the bike-wheel cell, validates its behavior by reproducing a well-established disjoining-pressure isotherm available in the literature, and briefly demonstrates the cell usefulness for protein and/or polymer stabilized aqueous foam films.

## **2. Bike-wheel film holder design and construction**

The operating principle of the bike-wheel microcell is similar to that of the Sheludko capillary.

However, due to the modified design, the dimensions of the capillary in which the film is formed are reduced 10-fold, while the dimensions of the pores through which solution drains are reduced 100-fold. Capillary pressures attained are comparable to those obtained with the porous-plate technique, and the film dimensions are closer to those encountered in actual foams and emulsions. Due to the miniaturization of the entire structure, drainage times necessary to observe thin, plane-parallel films are drastically reduced allowing the investigation of thin-film force laws as a function of time. This is particularly important for protein or polymer-based systems where significant aggregation within the film may occur with time, strongly influencing the rates of film drainage and coalescence. Moreover, the surface area in contact with protein or polymer solution is significantly decreased, rendering the loss of solute due to adsorption on the glass walls negligible and permitting investigation of chemical systems for which only small amounts are available. Bike-wheel microcells are easily cleaned and can, thus, be reused. Finally, multiple cells can be microfabricated simultaneously.

In short, the procedure for manufacturing bike-wheel microcells involves thermally bonding a chemically etched, flat-glass bottom substrate to a flat-glass top plate to form patterned flow channels. The entire procedure is summarized schematically in Fig. 1. Etched patterns are obtained by coating a bottom glass substrate with an amorphous silicon sacrificial layer, followed by spin coating with a photoresist film (steps 1 and 2). The channel pattern is transferred to the film by exposure to UV radiation through a patterning mask (step 3). Exposed portions of the film are dissolved (step 4), and the remaining film is hardened by heating. The subsequently exposed amorphous silicon layers are plasma etched (step 5) leaving an exposed pattern of bare glass substrate available for chemical etching (step 6). After wet etching of the glass substrate, the remaining photoresist and amorphous silicon are removed (step 7). Holes are then drilled prior to thermal bonding (step 8) of the etched substrate to the top glass plate.

Fig. 2 shows the dimensions and layout of a single microcell chip. Twenty-one microcells are fabricated simultaneously with each 4-in. diameter circular glass-wafer pair. Using diamond-coated bits ranging from 0.75 to 1.50 mm in diameter, multiple orifices are drilled through each glass-wafer (Borofloat<sup>®</sup> glass, 1-mm thick) to serve as microcapillaries where the thin-liquid films under study are formed. The orifices are tapered on the outside using a larger diameter drill to constrain film formation to the centerline [9]. The hole diameter and inner-edge thickness determine the minimum capillary pressure at which films can be formed [9]. A separate third orifice is drilled through the upper plate only of each microcell to serve as an outlet. The first orifice in the etched plate where the film is formed is connected by 24 shallow channels to an outer annulus of cross-dimensions 470- $\mu\text{m}$  wide by 50- $\mu\text{m}$  deep. These 24 shallow spoke channels are uniformly distributed

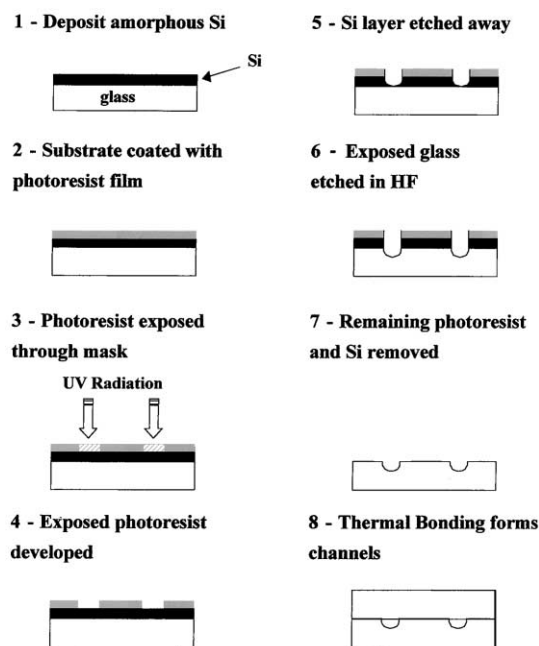


Fig. 1. Microfabrication of the bike-wheel film holder. Main steps include deposition of sacrificial layers and photolithography for transferring the desired pattern to the glass substrate followed by wet etching. The entire process must be repeated twice since the final etched pattern has channels of different depth. Drawing is not to scale.

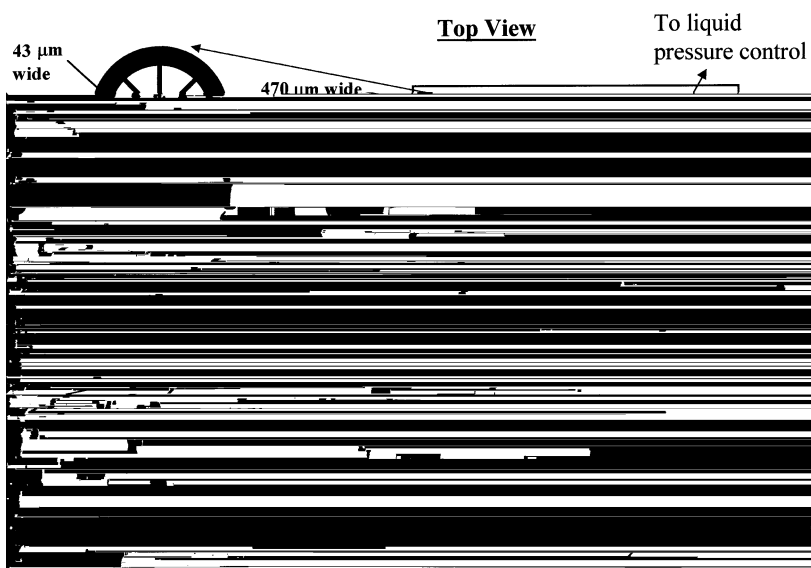


Fig. 2. Layout of the bike-wheel microcell. The film is formed in the center hole, and solution drains through shallow spoke channels responsible for a high entry pressure. The spoke channels are placed azimuthally around the film to ensure uniform flow. For clarity, only eight out of the 24 spoke channels are illustrated. Features are not drawn to scale.

azimuthally around the film orifice, forming the bike-wheel pattern and correcting for the unrealistic side-drainage typical of the conventional Sheludko capillary. The outer annulus extends into a 3-cm long channel connected to the third orifice in the upper plate, allowing for continuous entry or exit of the solution under study. Each spoke channel connected to the annulus is 43- $\mu\text{m}$  wide by 16- $\mu\text{m}$  deep, corresponding to an entry radius of about 8  $\mu\text{m}$  [10], which translates into an air/water entry pressure of about  $10^4$  Pa, close to what is obtained with the current porous-plate film holders. The spoke channels are only 1-mm long in order to minimize resistance to flow. Since the desired pattern presents two different depths, etching is a two-step operation where shallow portions are etched last and where two different masks are used.

Glass wafers are first cleaned with distilled and deionized water (DI  $\text{H}_2\text{O}$ ), submerged in a 120°C solution of a 4:1 v/v mixture of concentrated  $\text{H}_2\text{SO}_4$  (J.T. Baker, Phillipsburg, NJ) and  $\text{H}_2\text{O}_2$  (J.T. Baker, Phillipsburg, NJ), i.e. Piranha solution, for 15 min, and then thoroughly rinsed with DI water. The bottom glass wafer is dried in a

furnace at 150°C for 15 min, followed by deposition of 200 nm of amorphous silicon in a plasma chamber (Technics, UK) for 5 min at 40 W, 300°C, and 55 Pa using silane gas. The wafer is, thereafter, exposed to hexamethyldisilazane vapor for 5 min, coated with a layer of Microposit 1818 positive photoresist (Shipley, Newton, MA) on a Headway photoresist spinner (5000 rpm, 30 s), and then soft baked at 90°C for 25 min.

The photomask pattern was designed using the computer-assisted design software L-Edit (Tanner Research, Pasadena, CA) and manufactured by the Berkeley Microfabrication Laboratory with a GCA 3600F pattern generator and an APT chrome mask developer. The mask pattern is transferred to the substrate by exposing the photoresist to UV radiation (25  $\text{mW cm}^{-2}$  for ca. 10 s) through the mask in a Quintel contact printer and is then developed for one minute in a 1:1 (v/v) mixture of Microposit developer concentrate (Shipley, Newton, MA) and DI water. Next, in step 5 of Fig. 1, the amorphous silicon layer is plasma etched (Technics, UK) using  $\text{CF}_4$  gas at 200 W and room temperature leaving the patterned portions of the glass wafer bare. Finally,

the bottom glass plate is wet etched using concentrated HF (J.T. Baker, Phillipsburg, NJ). Etch depth is profiled with an Alphastep profilometer (Tencor, Mountain View, CA) and is controlled by monitoring the etch time. The etch rate for Borofloat glass is close to  $7 \mu\text{m min}^{-1}$ .

Following etching of the bottom glass wafer, the film of photoresist is removed by immersion in Piranha solution for 15 min. At this point the procedure outlined above is repeated with a different mask to transfer and etch the shallow portions of the pattern. Finally, the remaining amorphous silicon layer is plasma-etched away.

Prior to thermal bonding, the glass wafers are drilled and cleaned in Piranha solution for 15 min, rinsed thoroughly in DI water, dried with  $\text{N}_2$  gas, and then aligned under a microscope. Thermal bonding occurs in a Centurion Programmable Furnace (J.M. Ney Co., Yucaipa, CA) using the following temperature program: ramp  $10^\circ\text{C min}^{-1}$  to  $625^\circ\text{C}$ , hold for 3.5 h, and cool to room temperature. This heating and cooling cycle is based on the procedure of Wooley and Mathies [11]. Individual microcells are sliced from the bonded glass wafers using a spinning-diamond glasscutter wheel and thermally fused to a standard 4-mm OD glass capillary for mounting in the thin-film balance. A plan-view micrograph of the bike-wheel microcell is shown in Fig. 3.

Although it is technically possible to manufacture film holders with extremely small film diameters corresponding to emulsion- and foam-film sizes in actual emulsions and foams, we find this undesirable for two reasons related to the use of the thin-film interferometric method of Sheludko for the measurement of film thickness [1,2]. First, as the film diameter becomes smaller, dimple formation upon initial film formation is less pronounced making it very difficult to estimate the maximum in intensity that is necessary for calibration of the thickness measurements [1,2]. Without an accurate maximum in intensity, it is not possible to obtain reliable thickness measurements by the Sheludko optical procedure. Second, as the hole diameter decreases, significant stray reflections arising from the glass edges can be collected by the fiber-optic probe leading to artificially large thickness measurements. Typically, we employ

hole diameters in the 0.75–1.50 mm range and inner taper thicknesses of about  $100 \mu\text{m}$ . For such aspect ratios and for small capillary pressures, the Plateau border remains pinned at the taper edge as the film radius is expanded or contracted. Because the capillary pressure is gauged directly, it is not necessary to obtain precise measurements of the film radii [3,4,9].

### 3. Validation of bike-wheel film holder

We chose to validate the bike-wheel microcell by measuring the disjoining-pressure isotherm of 0.1 M sodium dodecylsulfate (Eastman Kodak, electrophoresis grade) aqueous foam films, using 1-day-old solutions. Bergeron and Radke previously investigated this system in detail using the porous-plate film holder [9]. They observed stratification behavior in the ultralow disjoining-pressure regime due to structural arrangement of the SDS micelles within the thin film. Upon increasing the capillary pressure, a layer of micelles is expelled corresponding to a change in film thickness equivalent to 10 nm, which is the pertinent effective micelle diameter at this concentration. This isotherm is of interest to us since data are

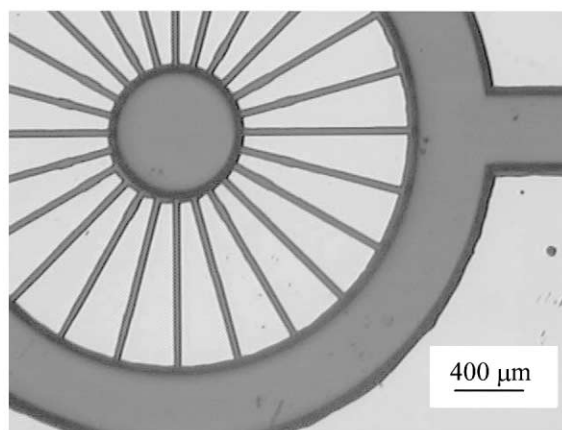


Fig. 3. Micrograph of the bike-wheel microcell upper plate. A bar indicates the size scale. Notice how the spoke channels connect the orifice where the thin film is formed (the hub) to the annulus (the wheel). Because the spoke channels are of a different depth and the image is focused on the annulus, it is not possible to observe the actual contact parts in detail.

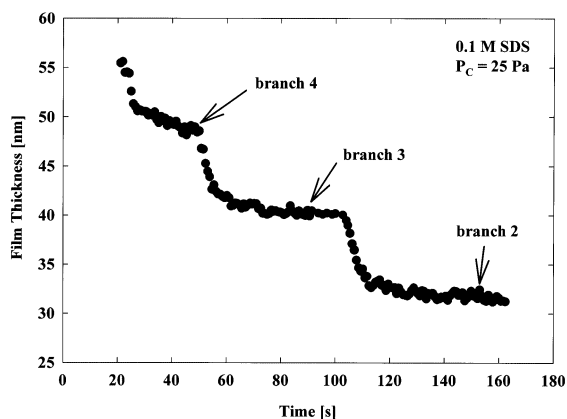


Fig. 4. Dynamic thinning of a 0.1 M SDS solution above the critical micelle concentration. This system has oscillatory behavior as it can be seen through the stepwise thinning, where each step corresponds to the effective hard-sphere size of one micelle layer. In this particular example, two film transitions are observed, counting from the outermost branch of the isotherm. Data are measured in a bike-wheel microcell with hole diameter equal to 1.25 mm at a capillary pressure corresponding to 25 Pa.

available both at extremely low values of the disjoining pressure, as well as at elevated ones, and film thicknesses span over a wide thickness range, including film transitions.

A typical example of the dynamic thinning of this SDS solution measured with the bike-wheel film holder is shown in Fig. 4. Arrows indicate films of different thicknesses corresponding to different numbers of micelle layers or isotherm branches. Branch numbering starts with the thickest film and proceeds inward corresponding to Fig. 6 to follow. Stratification is evidenced by the visually observed hole-sheeting events [12], as shown in Fig. 5, and by the abrupt step changes in thickness, as shown in Fig. 4. The film thins through stepwise changes until the last observed transition takes over the entire film and a final equilibrium thickness is attained corresponding to the imposed capillary pressure. Thus, we find that the bike-wheel microcell faithfully reproduces stratification behavior in micellar surfactant-stabilized foam films. In addition, thinning to an equilibrium plane-parallel film is readily achieved with the bike-wheel film holder even with extremely low applied capillary pressures due to the reduced dimensions of the entire assembly.

By careful variation of the applied capillary pressure, the entire disjoining-pressure isotherm can be mapped out. In Fig. 6, the disjoining-pressure isotherm measured with two different bike-wheel film holders is presented along with the data of Bergeron and Radke [9] taken with the porous-plate film holder. Numbers in parentheses refer to the hole diameter of the particular film holder. The isotherm is oscillatory displaying four observable branches in the ultralow-pressure regime. As discussed by Bergeron and Radke, an appropriate combination of hole and taper inner-edge thickness together with the surface tension of the solution under investigation, determines the minimum entry pressure at which a film can be formed in a specific film holder. With a bike-wheel cell of hole diameter equal to 1.25 mm and a typical taper inner-edge thickness of 100  $\mu\text{m}$ , we are able to measure the low values of the disjoining pressure seen in Fig. 6.

Our measurements are in good agreement with the values reported by Bergeron and Radke. No

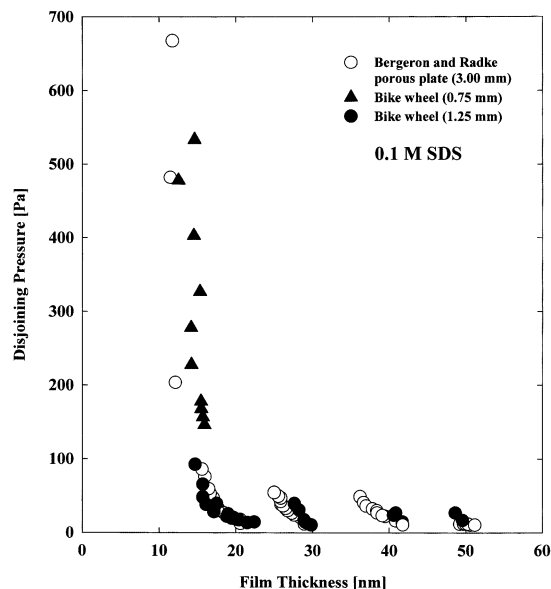


Fig. 6. Disjoining-pressure isotherm for 0.1 M SDS above the critical micelle concentration measured with bike-wheel microcells of different hole diameters, i.e. 0.75 and 1.25 mm. Measurements are in agreement with those of Bergeron and Radke [9] obtained with the porous-plate film holder. No dependence on the hole diameter is observed.

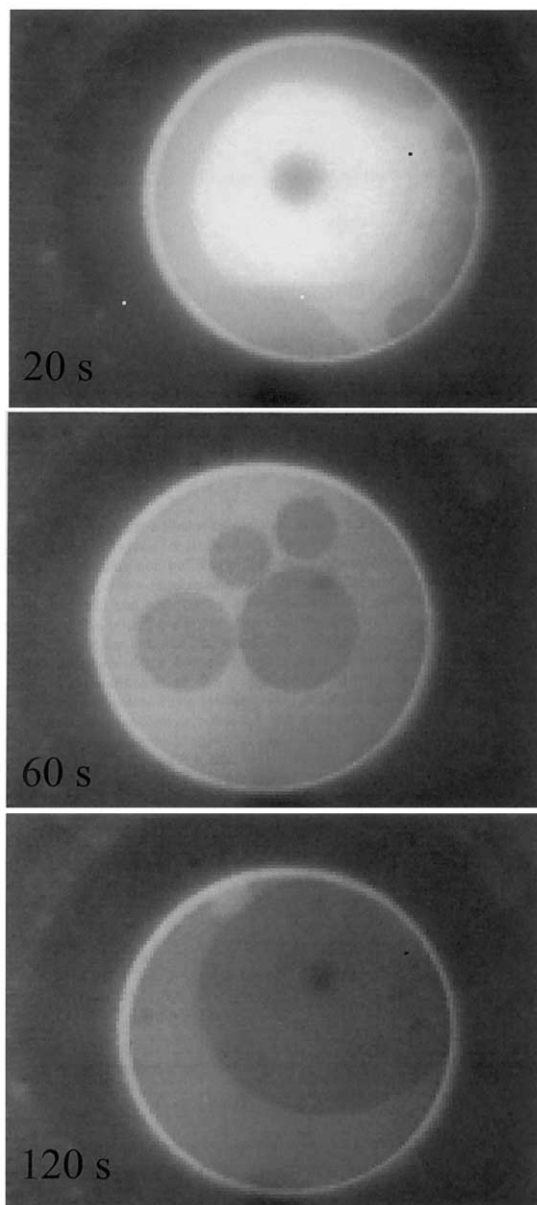


Fig. 5. Micrographs of dynamic thinning of a 0.1 M SDS solution above the critical micellar concentration in a bike-wheel microcell with hole diameter equal to 1.25 mm. Stratification is evidenced by the visually observed hole-sheeting events corresponding to films of different shades of gray.

distinction can be made between the measurements obtained with a porous-plate film holder and those with the new bike-wheel film holder. We focused on obtaining most data on the first

and second innermost branches, which are more readily accessible. However, points were obtained on all branches, and the thickness transitions correspond as expected to the effective micelle diameter. By carefully ramping the applied capillary pressure up and down, reversibility of a particular isotherm branch can be probed. No hysteresis is observed, and the thicknesses measured in Fig. 6 correspond to equilibrium films. We are able to maintain films at a given thickness on a given branch indefinitely provided environmental perturbations are damped. With a bike-wheel film holder having a hole diameter of 0.75 mm, disjoining pressures starting at 50 Pa only can be measured, thus, placing ourselves already on the common black branch. Once again, very good agreement is obtained with the data of Bergeron and Radke all the way up to high capillary pressures corresponding to several kPa. At high capillary pressures, a transition to a Newton black film is observed, but is not reported in Fig. 6 [9].

Disjoining-pressure isotherms measured with the bike-wheel film holders having different hole diameters overlap in those regions accessible to both. Bergeron and Radke used a porous-plate film holder with a hole diameter of about 3.0 mm for measurements in the ultralow-pressure regime [9,13]. No effect of film diameter on the measured values of the disjoining-pressure isotherm is observed with our bike-wheel cells of different hole diameters or with different types of film holders having different hole diameters. Accordingly, we assert that the bike-wheel microcell provides valid measurements of thin-film forces.

#### 4. Application to protein solutions

As a preliminary example of the generality of the bike-wheel cell, we measure the disjoining-pressure isotherm of bovine serum albumin (BSA). BSA is a well-characterized, large, rigid globular protein of approximate dimensions  $4 \times 4 \times 14 \text{ nm}^3$  corresponding to an ellipsoid [14]. It has a molecular weight of 69 kDa, an isoelectric point of 4.9, and was purchased from Sigma (A-0281), 99% pure with essentially no free fatty acid.

The disjoining-pressure isotherm of  $1.0 \text{ g l}^{-1}$  BSA is shown in Fig. 7, at pH 5.2 in  $1.0 \text{ mM}$  NaCl at  $22^\circ\text{C}$ . Protein-stabilized films are formed from a fresh aqueous solution aged no longer than 1 h. Initially, a thick biconcave lens is formed, and protein is allowed to adsorb for 20 min prior to measurement. The protein is not allowed to age at the interface for more than 30 min, after which fresh films are reformed. The observed isotherm in Fig. 7 is reversible and monotonic. Films are stable only at low values of the disjoining pressure, rupturing at capillary pressures above about 500 Pa. At pH = 5.2 there is very little charge on the protein, which is further screened by the indifferent electrolyte. BSA films are, therefore, most likely stabilized by repulsive steric forces [15]. The limiting thickness, which is reported assuming that the film has an index of refraction equal to that of pure water, is equal to  $12 \text{ nm}$  ( $\pm 1 \text{ nm}$ ). This value is close to an intervening protein bilayer assuming side-on adsorption or to an intervening protein monolayer assuming bridging between the film interfaces.

We find that protein film stability depends strongly on film history. As the BSA film ages,

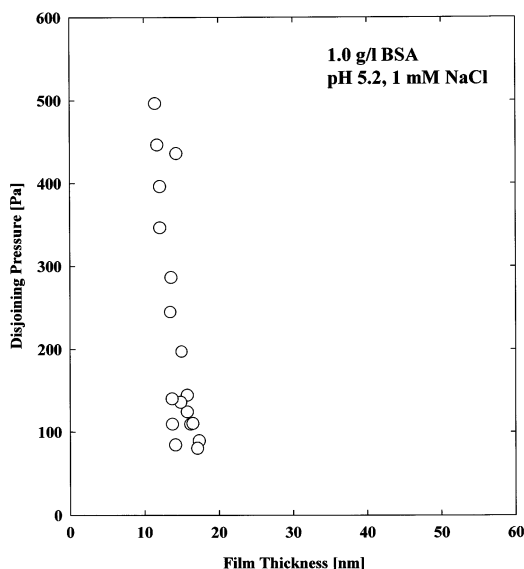


Fig. 7. Disjoining-pressure isotherm for  $1.0 \text{ g l}^{-1}$  BSA, pH 5.2,  $1 \text{ mM}$  NaCl at  $22^\circ\text{C}$ . Measured with a bike-wheel micro-cell of hole diameter  $1.50 \text{ mm}$ .

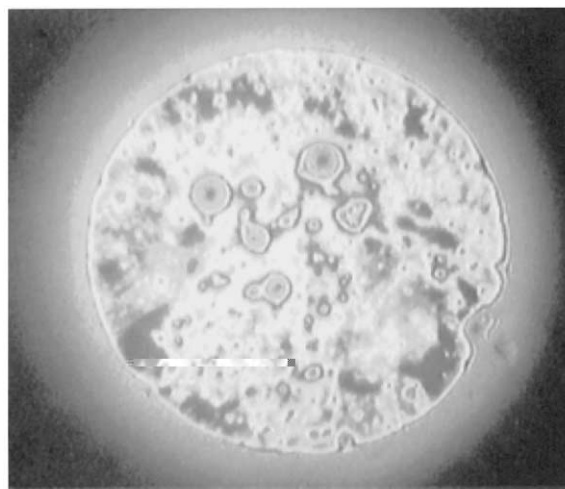


Fig. 8. Micrograph of a  $1.0 \text{ g l}^{-1}$  BSA foam film, pH 5.2,  $1 \text{ mM}$  NaCl at  $22^\circ\text{C}$  after aging for 2 h. The film is highly heterogeneous due to surface aggregation and will not thin further.

surface aggregation is observed, and the film becomes progressively more stable to higher applied capillary pressures. Fig. 8 illustrates a  $1.0 \text{ g l}^{-1}$  BSA film aged for 2 h as a biconcave lens before formation of a planar film. The film is rigid, mottled in appearance, and highly heterogeneous in thickness. It will not thin further. Film stability is no longer dictated by equilibrium thin-film forces alone, but primarily by the mechanical strength of the surface aggregates. Sedev et al. measured a disjoining-pressure isotherm for  $4 \text{ g l}^{-1}$  BSA foam films under similar conditions to ours using the porous-plate film holder [15]. They find a limiting thickness of about  $12 \text{ nm}$  at disjoining pressures close to  $10 \text{ kPa}$ , similar to Fig. 7. A more detailed comparison is hindered by the fact that these researchers employed a less pure BSA sample containing fatty acids, and no information is provided about the degree of aging of the films.

## 5. Conclusions

We have developed a new, microfabricated bike-wheel film holder for thin-film force measurements, which is a hybrid of the Mysels–Exe-

rowa–Sheludko porous-plate film holder and the conventional Sheludko capillary film holder. The bike-wheel film holder combines the advantages of the other two film holders currently used namely, a wide range of capillary pressures available for investigation, reusability, radial drainage, and low surface area permitting the investigation of proteins, polymers and specialty chemicals for which small amounts are available. The microfabrication procedure outlined currently allows for simultaneous manufacture of 21 bike-wheel cells.

Validation of the bike-wheel cell is established by measurement of the disjoining-pressure isotherm of 0.1 M SDS above the critical micelle concentration, previously measured by Bergeron and Radke employing a porous-plate film holder [9]. There is good agreement between the two isotherms both at low and high capillary pressures. No distinction can be made between measurements obtained with the bike-wheel cells of different hole diameters or between bike-wheel cells and the porous-plate holder of different hole diameters.

The disjoining-pressure isotherm is presented for 1.0 g l<sup>-1</sup> fatty-acid-free BSA fresh aqueous solutions at pH close to the isoelectric point. The isotherm of fresh BSA films is monotonically repulsive, and film rupture occurs at about 500 Pa. The limiting thickness is equal to 12 nm suggesting a film stabilized mainly by steric repulsive forces. Upon aging of the protein at the interface, surface aggregation is observed, and film stability is drastically enhanced. Aged BSA films are highly rigid and heterogeneous, and do not thin much beyond their initial state of formation. The mechanical strength of the aggregated film surfaces is apparently responsible for film stabilization rather than equilibrium thin-film forces. The new bike-wheel microcell proves very useful for the investigation of thin-film force laws, especially of films

stabilized by high-molecular-weight surfactant/polymer species, even those for which the degree of aging at the interface strongly influences film stability.

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## References

- [1] A. Sheludko, D. Exerowa, *Izv. Chim. Inst. Bulg. Akad. Nauk.* 7 (1959) 123.
- [2] A. Sheludko, *Adv. Colloid. Sci.* 1 (1967) 391.
- [3] P.M. Claesson, T. Ederth, V. Bergeron, M.W. Rutland, *Adv. Colloid Interface Sci.* 67 (1996) 119.
- [4] V. Bergeron, *Curr. Opin. Colloid Interface Sci.* 4 (4) (1999) 249.
- [5] K.J. Mysels, *J. Phys. Chem.* 68 (1964) 3441.
- [6] K.J. Mysels, M.N. Jones, *Disc. Far. Soc.* 42 (1966) 42.
- [7] D. Exerowa, A. Sheludko, *Comptes Rendus de l'Académie des Sciences* 24 (1) (1971) 25.
- [8] O.D. Velev, G.N. Constantinides, D.G. Avraam, A.C. Payatakes, R.P. Borwankar, *J. Colloid Interface Sci.* 175 (1) (1995) 68.
- [9] V. Bergeron, C.J. Radke, *Langmuir* 8 (12) (1992) 3020.
- [10] H. Wong, S. Morris, C.J. Radke, *J. Colloid Interface Sci.* 148 (2) (1992) 317.
- [11] A.T. Wooley, R.A. Mathies, *Proc. Natl. Acad. Sci. USA* 91 (24) (1994) 11348.
- [12] V. Bergeron, A.I. Jiménez-Laguna, C.J. Radke, *Langmuir* 8 (12) (1992) 3027.
- [13] V. Bergeron, Ph.D. Thesis, University of California, Berkeley, 1993.
- [14] T. Peters, *Adv. Protein Chem.* 37 (1985) 161.
- [15] R. Sedev, Z. Németh, R. Ivanova, D. Exerowa, *Colloid Surf. A. Physicochem. Eng. Asp.* 149 (1–3) (1999) 141.