A Novel Fast Technique for Measuring Dynamic Surface and Interfacial Tension of Surfactant Solutions at Constant Interfacial Area

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A novel, fast formed drop technique is developed for measuring dynamic surface and interfacial tension of surfactant solutions. It employs the basis of the capillary pressure methods. A new way of formation of a fresh interface is the key point in the proposed technique. It is based on the fact that a jet of liquid flowing out of a capillary breaks very fast after a sudden stop of the flow, but a small drop with a fresh interface remains at the capillary tip. Once the drop is formed, its size (and thereby its area) remains constant, while the capillary pressure is measured with a pressure transducer. The dynamic surface (or interfacial) tension is calculated by means of the Laplace equation for capillarity. In this way, measurements under constant interfacial area in a time domain from about 50 ms up to several minutes or more can be made. The measurements with pure liquids give constant values of the dynamic surface and interfacial tension equal to the corresponding equilibrium values reported in literature. The dynamic surface tension of Triton X 100 and Triton X 405 solutions measured by the new technique are in a good agreement with those obtained by the static drop weight method. The applicability of the new technique for measuring the dynamic interfacial tension is demonstrated. **© 1999 Academic Press**

Key Words: **fast formed drop technique; dynamic surface tension; dynamic interfacial tension; constant interfacial area; surfactant solutions.**

INTRODUCTION

Surfactant solutions play an essential role in many industrial processes such as foaming, froth flotation, emulsification, and detergency. The practical importance of the surfactants is based on the ability of their molecules to accumulate at freshly created solution/fluid interfaces, thus decreasing the surface or interfacial tension. The latter quantities, being a measure for the specific free surface energy, change continuously with time until their equilibrium values are reached. The nonequilibrium, transient values are called dynamic surface tension (DST) in the case of solution/gas interface or dynamic interfacial tension

(DIT) in the case of solution/liquid interface. Both, DST and DIT are related to the rate of transfer of the surfactant molecules from the bulk of solution onto the interface. The studies of the DST and the DIT give information not only for the adsorption rate but also for the mechanism of adsorption of surfactant molecules, thus helping to reveal the factors governing the adsorption process. That is why studies of DST and DIT are an important step in almost every scientific or applied investigation dealing with surfactant solutions.

Besides the chemical nature of the surfactant, the surfactant concentration has a strong effect on the DST and the DIT. The equilibrium surface (interfacial) tension of commonly used concentrated surfactant solutions is usually reached during the first several seconds after formation of a fresh interface. This requires fast experimental methods for measuring the DST and DIT to be used. An overview of the experimental methods can be found in Ref. (1).

Two groups of methods can be distinguished, depending on the expansion of the interface during measurements. These are (i) methods for measuring the DST (DIT) *at constant interfacial area* and (ii) methods involving *surface expansion.* The interpretation of the results obtained by the latter methods is much more difficult in comparison with the former. Indeed, the expansion of an interface always causes some convection fluxes inside the bulk phases (2), hence convective terms must be included in the governing equations of the adsorption problem. As a consequence, a general analytical solution of the adsorption problem can not be obtained and the latter has to be solved numerically (1, 3). Besides, the rate of surface expansion should be exactly known for the proper interpretation of the results. This requires more sophisticated equipment to be used (e.g., video recording, image analysis (4–6)) or some additional assumptions and approximations to be done in order to reduce the problem for adsorption with surface expansion to the case of adsorption at constant surface area (7, 8). These are disadvantages of all methods which employ expanding interfaces in comparison to the methods without surface expansion.

There are several methods for measuring the DST (DIT) *at constant interfacial area.* The classical Wilhelmy plate and du Noüy ring methods have a broad time domain, but both meth-

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ods are too slow to measure the DST (DIT) during the first several seconds after formation of a fresh interface. The methods involving hydrodynamic flow, like the oscillating jet (9, 10) and the inclined plate (11), are fast but have narrow time domains of measurements equal to 3 −50 ms and 0.05–2 s, respectively. Another disadvantage of the above two methods is they are applicable only at the solution/air interface. The latter limitation does not concern methods involving a drop attached to a tip of the capillary. These are the static drop volume (weight) (12–15), the pendent drop digitization (16), and the expanded drop (17, 26, 27) methods. The DST (DIT) is calculated by use of the volume (or the weight) of the drop detached from the capillary tip in the first of the methods. The second one uses for that purpose the drop profile obtained by an image analysis of the drop shape. The directly measured capillary pressure of the drop is used for calculation of the DST (DIT) in the expanded drop method. The measuring procedure of these methods consists of two consecutive stages, (i) formation of a "fresh" drop at the tip of the capillary by squeezing out a solution by means of a syringe, and (ii) measuring the DST (DIT), $\sigma(t)$, as a function of the surface age, t, under constant volume of the drop. The end of the first stage is assumed to be the beginning of the adsorption process ($t = 0$); i.e., the surfactant does not adsorb at the drop surface during the stage of drop formation. This assumption should be more valid at small adsorption rates (e.g., in diluted solutions) and at short duration of the drop formation stage. The stage of drop formation lasts from several tenths of a second up to several seconds in the static drop volume and the pendent drop digitization methods. That is why both methods are not appropriate for measuring the DST (DIT) when the characteristic adsorption time is smaller than several seconds. More over, the adsorption of the surfactant during the drop formation stage can not be neglected, especially in the case of concentrated solutions. For that reason some authors claimed that the data obtained by the static drop volume method at short times could not be properly interpreted (15). The problems discussed above are overcome to some extent by Liggieri *et al.* (17, 26, 27), who proposed the expanded drop technique. This technique belongs to a group of so-called capillary pressure methods (for an overview see Ref. (26)). They all are based on direct measurement of the capillary pressure, P_c, of a drop attached to a tip of a capillary. Precise pressure transducers for that purpose are used. The surface (interfacial) tension, σ, is calculated by means of the Laplace equation for capillarity, which in the case of a sphere with radius R reads

$$P_c = \frac{2\sigma}{R}. \qquad [1]$$

This equation is strictly valid in a special case of zero Bond number (i.e., under zero gravity or zero difference between densities of the drop liquid and the surrounding fluid). At small

drops and/or a small density difference Eq. [1] still can be used without significant error.

During last decade different modifications of capillary pressure methods were developed, first by Passerone *et al.* (18) and later by others (4, 5, 17, 19, 26, 27). The expanded drop technique (17, 27) differs from the other capillary pressure methods by the fast drop expansion occurring in a few tenths of a second. The fast expansion in the earlier version of this technique (17) is obtained by suitable value of the capillary tip and by introducing a gas volume in the system. Under certain conditions, the presence of the gas bubble provides an unstable state for the system during the drop formation. In fact, in this case, after the drop has reached the hemispherical shape, a sudden increase in its volume is observed. The drop area increases more than 20 times in a short time. In this way a large drop with "fresh" surface is formed at the capillary tip. However, the introduction of a gas volume in the system leads to some negative effects related to change of the drop size during measurements and to an increased sensitivity of the system toward temperature fluctuations. These negative effects are eliminated in the recently developed upgraded version of the expanded drop technique (26, 27). The major improvement is the use of a piezoelectric piston for the expansion of the drop, thus allowing a 50-fold increase of the drop area to be achieved within 0.2 s.

In summary, only a few experimental methods allow measurements the DST (DIT) during the first second after formation of a fresh interface. Some of them have a narrow time domain of measurement and are applicable to solution/gas interfaces only. Other methods involve a surface expansion, which complicates the interpretation of the results. The above disadvantages are overcome to a large extent in the expanded drop method (17, 26, 27). An alternative of the latter method based on a totally different principle for formation of a fresh interface is proposed in the present work.

The experimental technique developed by us employs the advantages of the capillary pressure methods—simple and clear theoretical backgrounds (see Eq. [1]), fast and easy acquisition of a large amount of experimental data, and suitability for DIT and DST measurements. The key point is the way of forming a fresh interface. In contrast to the expanded drop technique, we use the fact that a jet of liquid flowing out of a capillary breaks very fast after a sudden stop of the flow, but a small drop with a fresh interface remains at the capillary tip. That is why we call the new technique *"a fast formed drop" (FFD) technique.* Once the drop is formed, its size (and thereby its area) remains constant, while the capillary pressure is measured with a pressure transducer. The dynamic surface (or interfacial) tension is calculated by means of Eq. [1]. The experimental setup, the experimental procedure, and the way of calculating the DST (DIT) are described in detail in the next three sections, together with the results of tests with pure liquids. Since the static drop weight method was used as a referent method for some of the DST measurements, it is
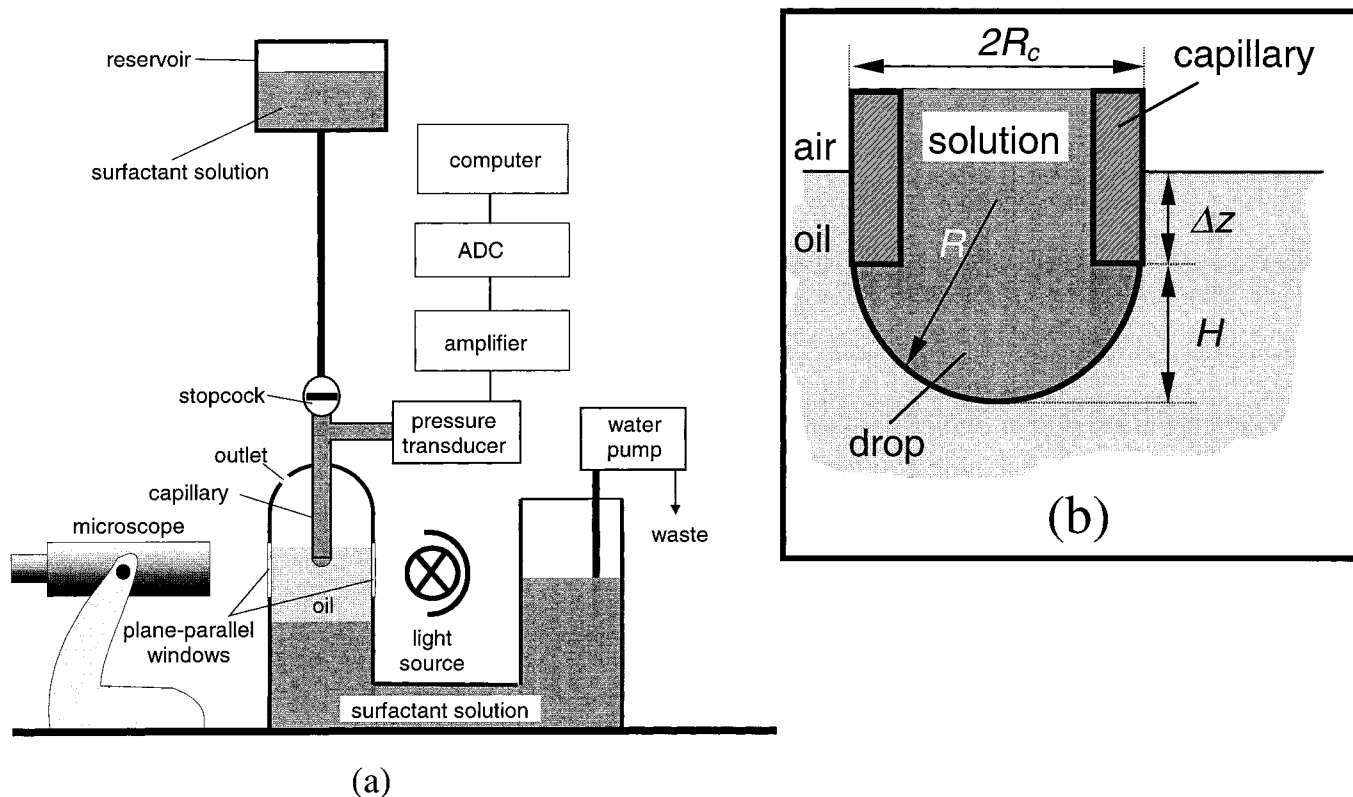
FIG. 1. Sketch of the experimental setup (a) and close-up of the capillary tip (b).

briefly described in Materials and Methods. The obtained results with surfactant solutions are discussed, and some conclusions are drawn in the last two sections of the work.

EXPERIMENTAL SETUP

A sketch of the experimental setup is shown in Fig. 1. One end of a glass capillary with outer radius $R_c = 0.0659 \pm 0.0001$ cm is connected to a reservoir of surfactant solution and to a pressure transducer (Omega, type PX163-005BD5V). The level of the solution in the reservoir is approximately 80 cm above the capillary tip. A stopcock is mounted in the plastic pipeline not far from the capillary. When the stopcock is closed the transducer can measure the pressure inside the compartment with the capillary. The output signal of the transducer is amplified and, by means of an Analogue-to-Digital Converter (ADC), is stored in the PC. The ADC can convert analogue signals in the range $-5V–+5V$ with a precision of 0.1 mV. The sampling frequency range from 100 to 200 measurements per second was found to be most suitable. The time is measured by the PC's clock and is recorded as well. The capillary is mounted inside the left branch of a "U" shaped vessel partially filled with solution. When the stopcock is open, the solution flows out of the reservoir through the capillary as a jet. The level of the liquid in the left branch of the vessel can be

kept constant by sucking out the incoming solution from the right branch by means of a water pump. The drop remaining at the capillary tip after the flow is stopped is observed with a long-focus microscope. Plane-parallel windows are mounted inside the wall of the vessel for better observation.

EXPERIMENTAL PROCEDURE

The reservoir, the pipelines, and the capillary are filled with the surfactant solution. All air bubbles (even very small ones) should be removed, because they can compromise the measurements. For that reason, it is preferable to use deaerated water for preparation of the solutions. First, the referent output voltage, U_0, of the pressure transducer has to be determined, before measurements are made. For that purpose a slightly convex meniscus is formed at the capillary tip. Then, the level of the solution in the "U" shaped vessel is elevated by addition of solution to the right branch until the capillary tip is touched by the surface of the solution. The output voltage of the transducer at that moment, U_0, corresponds to a flat surface at the tip of the capillary.

Dynamic Surface Tension Measurements

The level of the solution is adjusted to be several centimeters below the capillary tip by sucking out the liquid from the right
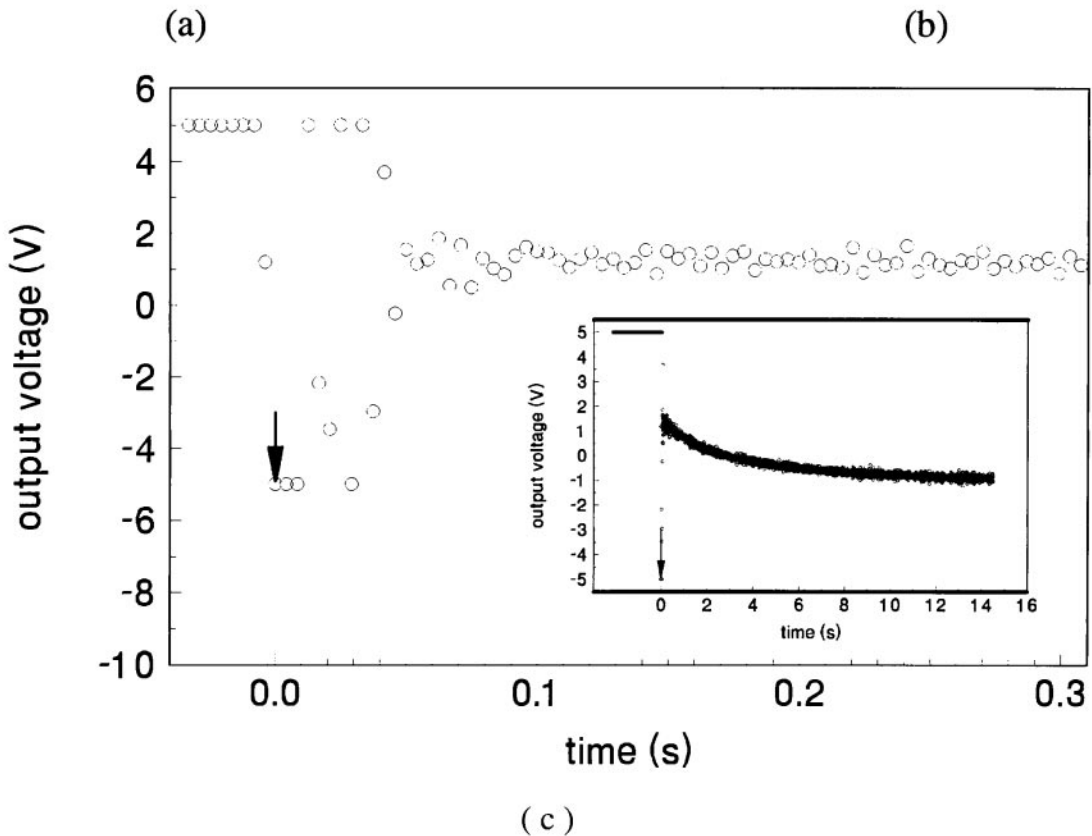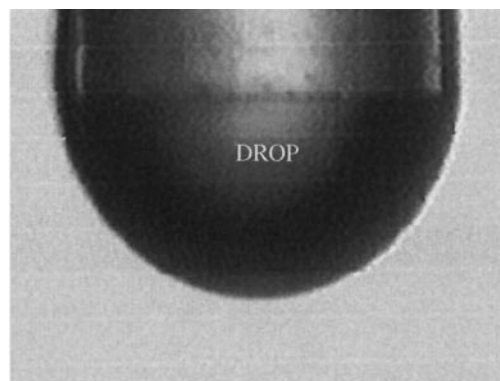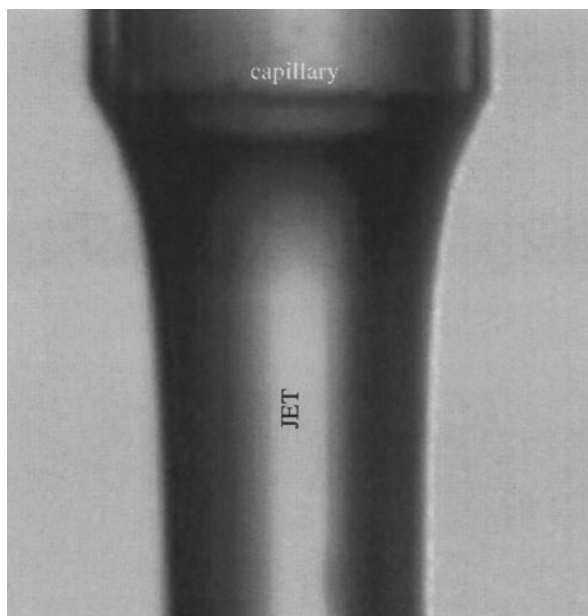
(a)

(b)

(c)

FIG. 2. Photographs of liquid flowing out of a capillary as a jet (a), the drop remaining at the capillary tip after the flow was stopped (b), and a plot of respective changes of the output voltage of the pressure transducer with time (c). Arrows denote the moment when the jet breaks.

branch of the "U"-shaped vessel. Then, the stopcock is opened and the surfactant solution flows out of the capillary as a jet (Fig. 2a). Since the applied pressure is high, the output voltage is constant and equal to the upper limit of the ADC (Fig. 2c).

About 10 s later, the stopcock is suddenly closed, the flow stops, and an almost hemispherical drop is formed at the capillary tip (Fig. 2b). We found out by video recording that the jet breaks in less than 33 ms (one video frame), hence the

drop with a fresh surface is formed very fast. It is worth noting that the drop formation stage in the proposed technique is about 10 to 100 times shorter than that in the methods discussed in the beginning of the present paper. The moment of flow arrest is well visible in Fig. 2c, where a typical change of the output voltage with time is shown. The flow breaking off causes a sharp decrease of the pressure due to the hydrodynamic shock (so-called water hammer), so the output voltage falls from its upper to its lower limit (see the arrow in Fig. 2c). We take this moment as the beginning of the measurement of the DST ($t = 0$). This point is followed by damped oscillations of the output signal. Approximately 30–50 ms after the flow is arrested, the output voltage calms down and starts to follow the trend of the pressure inside the drop. The highly scattered data collected during the early stages of the measurements were eliminated, but the rest of the data obtained at times larger than 40–50 ms were taken into account. Hence, the lower time limit of measurements by the proposed technique is as short as approximately 50 ms. There is not a limitation for the duration of the measurements, if the temperature of the system is kept constant to assure constant size of the drop. We have found out that the drop size was practically constant during the first several minutes of the experiments even without precise temperature control. That is why we have restricted the duration of our measurements to about 300 s. The latter restriction can be eliminated if the temperature of the system is kept constant with an accuracy 0.1°C (or better) by means of a thermostat. The drop height, H, (Fig. 1b) is measured by a horizontal microscope with an accuracy of 6 μm. Then the dynamic surface tension is calculated in the way described in the next section.

If the DST against vapors of some oil is of interest, a small amount of oil is added over the solution through the outlet of the "U" shaped vessel (see Fig. 1a). After some time, the atmosphere around the capillary is saturated with oil vapors and the DST is measured in the way described above.

Dynamic Interfacial Tension Measurements

The oil phase is added through the outlet of the "U" shaped vessel in such an amount to form a several centimeters thick oil layer over the solution (see Fig. 1a). Some quantity of the solution is sucked out by the water pump until the depth of immersion, Δz, of the capillary inside the oil becomes equal to several millimeters (see Fig. 1b). After that, the same procedure as for DST measurements is followed. Beside the drop height, H, the depth of immersion, Δz, is also measured by the microscope with an accuracy 25 μm. Then the DIT is calculated (see below).

CALCULATIONS OF THE DST AND THE DIT

The capillary pressure, P_c, is defined as a difference between the pressure inside, P_{in}, and the pressure outside the drop, P_{out}; i.e.,

$$P_c = P_{in} - P_{out}. \qquad [2]$$

On the other hand, there is a linear relation between the applied pressure and the output voltage of the pressure transducer used by us. Hence, we can write

$$\Delta P = \frac{\partial P}{\partial U} \Delta U, \qquad [3]$$

where $\partial P / \partial U$ is a constant for a given feed voltage of the transducer. Having this in mind, and taking into account that P_{out} is practically equal to the pressure at the flat solution/air interface, we can express the capillary pressure of the drop attached at the capillary tip as a function of the measured output voltage

$$P_c = \frac{\partial P}{\partial U} (U - U_0), \qquad [4]$$

where the output voltage U corresponds to the drop, whereas U_0 corresponds to a flat solution/air interface. The latter quantity is determined in the beginning of each experiment in the way described in the previous section. In the case of solution/oil interface the hydrostatic pressure due to the immersion of the capillary tip in oil phase has to be subtracted from the right-hand side of Eq. [4]. The drop in our case is small and can be considered as a spherical segment with radius R. It can be calculated from the drop height, H, by the formula

$$R = \frac{H^2 + R_c^2}{2H}, \qquad [5]$$

where R_c is the radius of the capillary tip (Fig. 1b). Finally, from Eqs. [1], [4], and [5] we obtain

$$\sigma(t) = \left\{ \frac{\partial P}{\partial U} [U(t) - U_0] - \Delta\rho g \Delta z \right\} \frac{H^2 + R_c^2}{4H}, \qquad [6]$$

where $U(t)$ and $\sigma(t)$ are the output voltage of the transducer and the dynamic surface tension at time t, respectively, $\Delta\rho g \Delta z$ is the hydrostatic term, $\Delta\rho$ is the difference between the densities of the drop liquid and the surrounding fluid, and g is the gravity. The depth of immersion of the capillary tip, Δz, is settled to zero in the case of solution/gas interface. Since U_0, $U(t)$, Δz, H, and R_c are experimentally measured, the DST or the DIT can be calculated by Eq. [6]. The constant $\partial P / \partial U$ needed for these calculations has been preliminarily determined by experiments with pure water, the surface tension of which is known to be equal to 72.2 dyn/cm at 24°C (20). Equation [6] was used for that purpose. We have found out $\partial P / \partial U = 450 \pm 1.4$ dyn/cm^2 per volt. In order to verify this value we have measured the DIT of pure water against pure
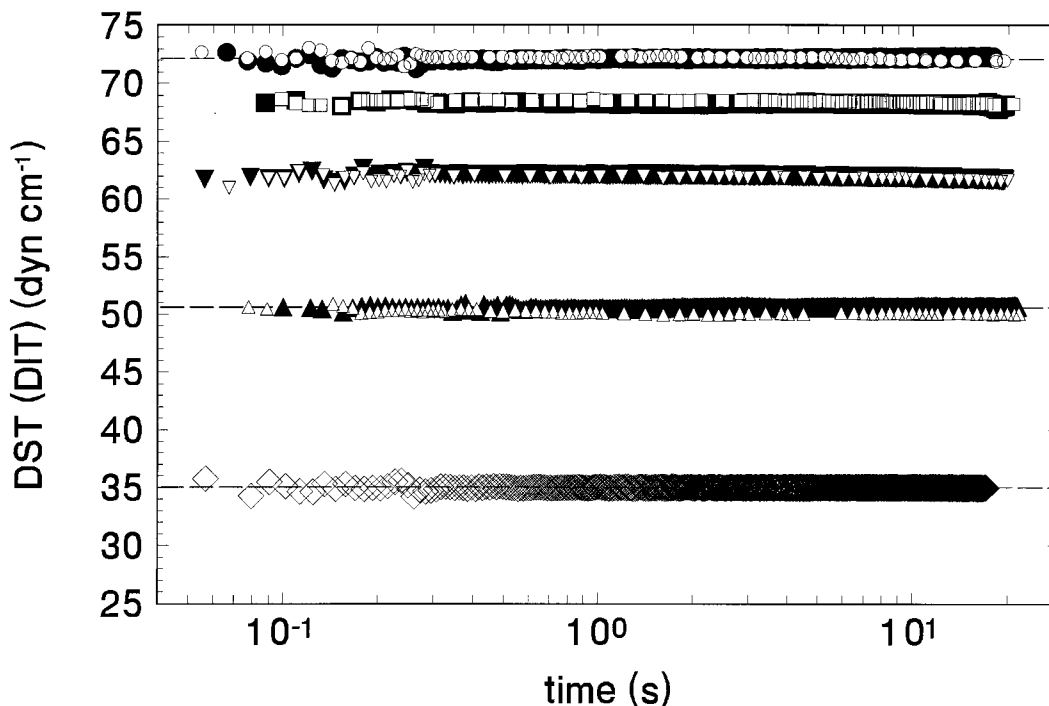
FIG. 3. Dynamic surface tension of pure water against air ($\bigcirc$, $\bullet$), hexane vapors ($\square$, $\blacksquare$), and benzene vapors ($\triangledown$, $\blacktriangledown$), and dynamic interfacial tension of pure water against hexane ($\triangle$, $\blacktriangle$) and benzene ($\diamondsuit$) measured by the FFD technique. Solid and empty figures correspond to different runs. The lines correspond to the respective equilibrium values taken from the literature (see Table 1).

hexane and benzene. The DST of pure water against vapors of hexane and benzene was also measured. The results are shown in Fig. 3 and in Table 1, where the obtained DST and DIT values are compared with the equilibrium values known from the literature. As it should be, the DST and DIT of the pure liquids are constant and coincide with the equilibrium literature values in the range of experimental error. The reproducibility of the results obtained from different runs is very good, as can be seen in Fig. 3. The surface tension of water against saturated vapors of hexane and benzene is lower than that against air, which seems a reasonable result. These results confirm the

correctness of the preliminarily determined $\partial P / \partial U$ value and the reliability of the experimental procedure. They also show that the assumption for the sphericity of the drop is fulfilled in the proposed technique; hence Eq. [1] can be directly applied. The error of the DST (DIT) values calculated by means of Eq. [6] is smaller than 0.5% (see Appendix A).

MATERIALS AND METHODS

The surfactants used in the present study were Triton X-100 and Triton X-405, both purchased from Serva. They are octyl-phenyl polyoxyethylene ethers with 10 and 40 oxyethylene groups, respectively. Both surfactants were used without further purification. Benzene (Sigma, spectroscopy grade) and n-hexane (Aldrich, 99% purity) were used in DIT measurements. Deaerated water was used in all experiments. For that purpose deionized water obtained with a Millipore unit was kept at 60°C under vacuum and continuous agitation by magnetic stirrer for about 1 h. Then, the water was chilled to room temperature and used for preparation of the solutions.

The new FFD technique was used for measurement of the DST of Triton X-100 and Triton X-405 solutions. The DIT of Triton X-405 solutions against n-hexane was also studied. The water phase was not preliminarily saturated with oil in these experiments and vice versa.

Some measurements of the DST of Triton solutions have

TABLE 1
Surface and Interfacial Tensions of Pure Water Measured by the Fast Formed Drop Technique at 24°C

| | σ (dyn cm^{-1}) | |
Second fluid	Measured	Literature
Air	72.2 ± 0.2	72.2[a]
Hexane vapors	68.3 ± 0.2	—
Benzene vapors	61.8 ± 0.2	—
Hexane	50.4 ± 0.2	50.6[b]
Benzene	35.2 ± 0.2	35.0[b]

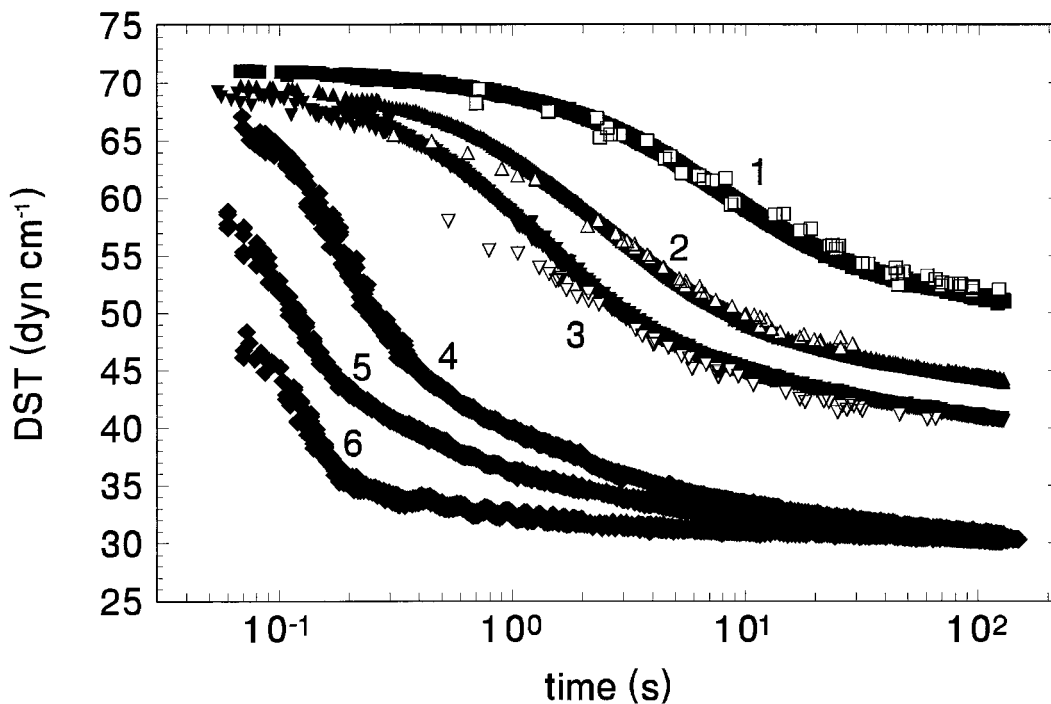[a] Taken from Ref. (20).
[b] Taken from Ref. (24).

FIG. 4. Dynamic surface tension of Triton X 100 solutions measured by the FFD technique (solid figures) and by the static drop weight method (empty figures) at concentrations ($\times 10^8$ mol cm^{-3}) equal to 2.58 (1, $\square$), 5.0 (2, $\triangle$), 7.5 (3, $\triangledown$), 23.25 (4), 31.0 (5), and 62.0 (6).

been made by the static drop weight method, in order to be compared with the results from the FFD technique. For that purpose the experimental setup shown in Fig. 1 was modified in the following way. The microscope and the "U" shaped vessel were removed. The capillary was replaced by a much wider one, with outer radius equal to 0.4025 cm. The pressure transducer was removed and a syringe supplied with a motor driven piston was connected at the same place. The static drop weight experiments were performed in the following manner. The syringe was filled with a certain amount of surfactant solution. The stopcock was opened and the solution flowed out through the capillary as a jet. About 10 s later, the stopcock was closed and the flow stopped. Then the motor was turned on. It squeezed the solution out of the syringe to form a large drop pending at the capillary tip and automatically turned off. In contrast to the measurements with FFD technique, the time needed for formation of the drop in these experiments was much longer. It varied from about 0.3 s for the smallest drops to about 0.7 s for the largest. Once the drop was formed at the capillary tip, the motor was switched off and a chronometer was turned on. The time for detachment of the drop, t, was measured. The detached drop was collected in a Petri dish and its weight was measured by a "Sartorius" balance with a precision of 0.0001 g. The corresponding DST was calculated by the formula

$$\sigma(t) = \frac{W}{2\pi R_c \psi}, \qquad [7]$$

where $W = \Delta\rho mg$ is the drop weight, m being its mass, and ψ is the so-called Harkins and Brown correction factor (21). The ψ was calculated from the equation (22)

$$\psi = 0.9054 - 0.7249\left(\frac{R_c}{V^{1/3}}\right) + 0.4293\left(\frac{R_c}{V^{1/3}}\right)^2. \qquad [8]$$

Here, $V = W/\Delta\rho g$ is the volume of the detached drop, which was calculated from the drop weight assuming $\Delta\rho = 1$ g/cm^3. Different drop weights (hence different DST values) corresponding to adsorption times in the range from 0.3 s to several minutes were achieved by varying the volume of the solution squeezed out from the syringe.

All experiments were performed at room temperature (24°C).

RESULTS AND DISCUSSION

DST and DIT of Surfactant Solutions

The DST of Triton X 100 and Triton X 405 solutions are plotted in Figs. 4 and 5, respectively. The data obtained by the FFD technique (solid figures) are collected from at least 4 runs at each surfactant concentration and confirm the good reproducibility of the measurements. The DST of both surfactants tends to the surface tension of pure water at short times. This fact is evidence that the way of drop formation used in the FFD technique assures an initially (i.e., at $t = 0$) fresh drop surface.
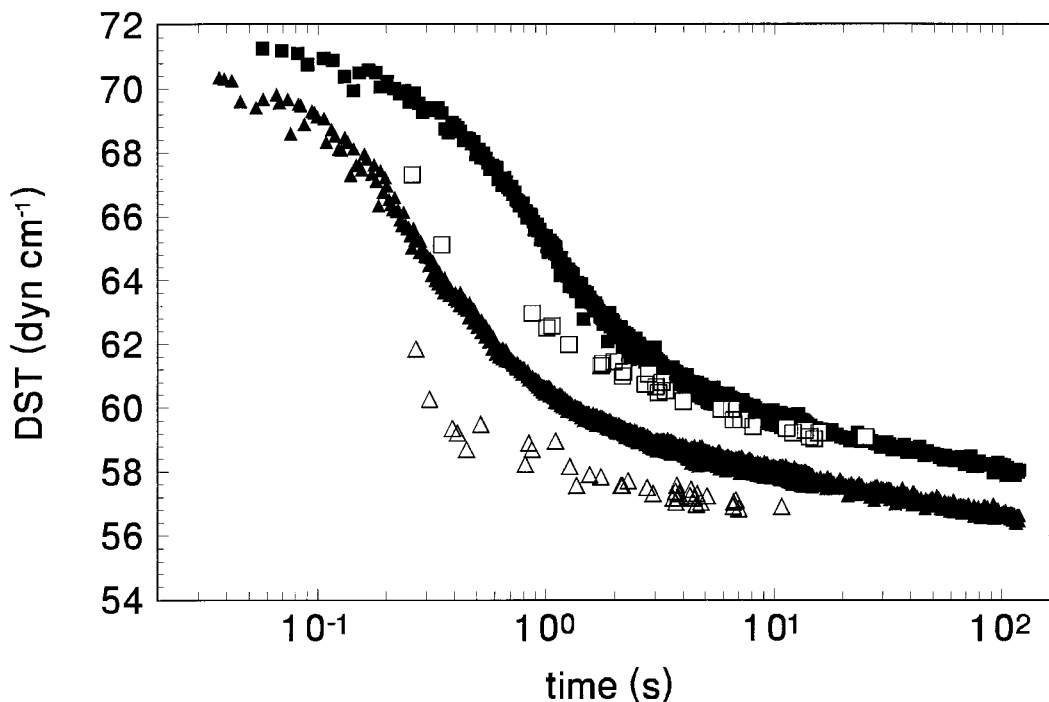
FIG. 5. Dynamic surface tension of Triton X 405 solutions measured by the FFD technique (solid figures) and by the static drop weight method (empty figures) at concentrations ($\times 10^8$ mol cm^{-3}) equal to 2.5 ($\blacksquare$, $\square$) and 5.0 ($\blacktriangle$, $\triangle$).

The DST of the most concentrated Triton X 100 solutions (curves 4–6 in Fig. 4) tend to one and the same value at long times. This is not unexpected, since all three concentrations are greater than the critical micelle concentration (CMC) of Triton X 100 (16, 23).

The dynamic interfacial tension of Triton X 405 solutions against *n*-hexane is plotted in Fig. 6. These data prove that the DIT of surfactant solutions can be measured by the FFD technique at times as short as 40–50 ms. The DIT may be influenced by a mass transfer through the drop interface, because both phases were not mutually saturated in these experiments. Nevertheless, the DIT tend to the interfacial tension of the surfactant free system water/hexane at short times (see Table 1), while they tend to the respective equilibrium values at long times (see the arrows in Fig. 6).

Comparison with Other Experimental Methods

The data measured by the static drop weight method are shown in Figs. 4 and 5 (empty figures) for comparison. Figures 4 and 5 illustrate very well some of the advantages of the new FDD technique, namely, the possibility for measurements at much shorter times and an easy accumulation of a large amount of experimental data. In the case of Triton X 100 the DST measured by the static drop weight method practically coincides with that measured with the FFD technique at times larger than 2 s. However, the static drop weight method gives lower DST values at short times. The difference increases with the increase of Triton X 100 concentration. This effect is better pronounced in the case of Triton X 405 solutions. These discrepancies can be attributed to the greater initial adsorption of the surfactants in the static drop weight experiments compared to that in the FFD measurements. Indeed, due to the much longer drop formation stage the drop surface in the static drop weight measurements is "less fresh" compared to the FFD technique, thus leading to lower initial DST values. The initial adsorption, however, has a weak effect at long times and the DST measured by both methods merge to one and the same curve. Due to the very fast formation of a fresh interface the FFD technique can be used for the adsorption kinetics studies of concentrated surfactant solutions. The obtained DSTs of micellar Triton X 100 solutions support this conclusion (see curves 4–6 in Fig. 4).

The new FFD technique differs from the expanded drop technique (17, 26, 27) by the manner of formation of a fresh interface. As a result, the following advantages of the former are achieved: The drop formation is much shorter (less than 33 ms instead of a few tenths of a second). This should lead to a fresher interface, especially in the case of concentrated solutions. The drops used in the FFD technique are smaller than those in the expanded drop technique. Hence, their shape is less affected by gravity and can be well approximated as a part of a sphere even in the case of large difference between densities of the drop liquid and the surrounding fluid (see Appendix B).
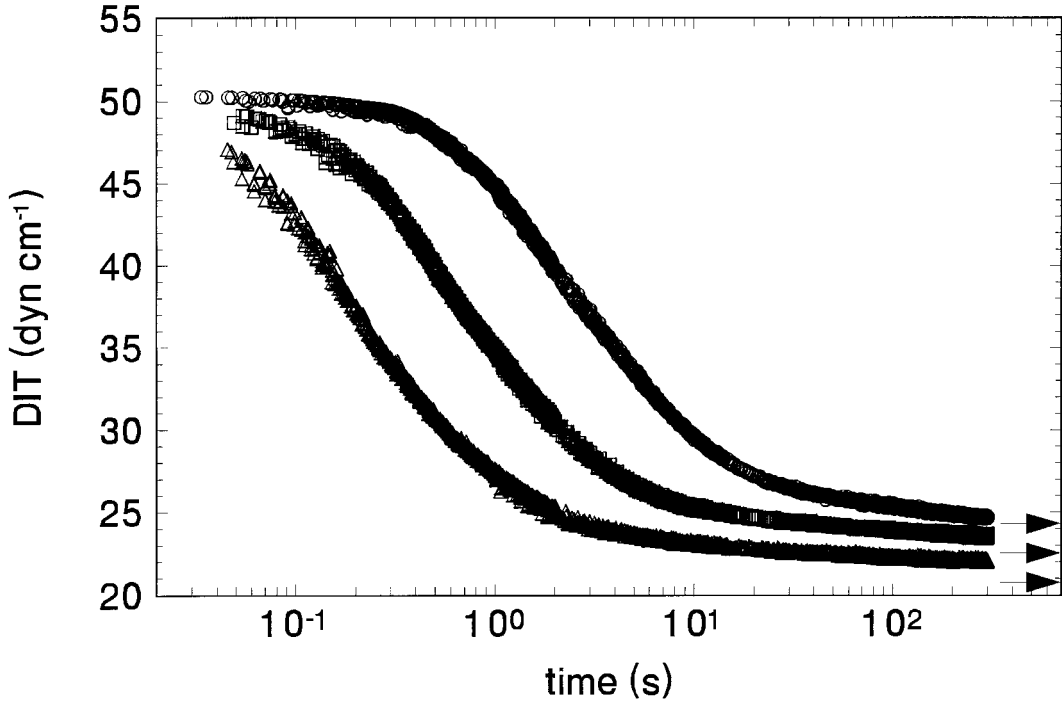
FIG. 6. Dynamic interfacial tension of Triton X 405 solutions against hexane measured by the FFD technique at concentrations ($\times 10^8$ mol cm^{-3}) equal to 1.25 ($\bigcirc$), 2.5 ($\square$), and 5.0 ($\triangle$). The arrows show the respective equilibrium interfacial tensions taken from Ref. (25).

CONCLUSIONS

A novel, so-called fast formed drop (FFD) technique is developed. It allows very reproducible measurements of DST and DIT of pure liquids and surfactant solutions to be made at constant interfacial area. The obtained results with pure liquids are in excellent agreement with the equilibrium data published in the literature. The FFD technique gives consistent data for the DST of Triton X 100 and Triton X 405 solutions. The results are in good agreement with those obtained by the static drop weight method. The FFD technique is equally applicable for measuring the DST and the DIT of diluted and concentrated surfactant solutions. The following advantages of the FFD technique in comparison to other experimental methods can be noted: simple and clear theoretical backgrounds, suitability for DIT and DST measurements in a broad time domain from about 50 ms to several minutes and more, fast and easy acquisition of a large amount of experimental data under constant interfacial area without need of video recording or image analysis, and easier interpretation of the results.

APPENDIX A: AN ESTIMATION OF THE ERRORS IN CALCULATIONS OF THE DST (DIT)

In general, the absolute error of a function $y = y(x_i)$ can be calculated by the formula (28)

$$\epsilon_y = \left[\sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i} \epsilon_{x_i} \right)^2 \right]^{1/2}, \qquad [A.1]$$

where ϵ_y is the absolute error of the function, n is the total number of the variables, x_i, and ϵ_{x_i} are their absolute errors. Applying Eq. [A.1] to Eq. [1] we obtain

$$\frac{\epsilon_\sigma}{\sigma} = \left[\left(\frac{\epsilon_R}{R} \right)^2 + \left(\frac{\epsilon_{P_c}}{P_c} \right)^2 \right]^{1/2}, \qquad [A.2]$$

where ϵ_σ/σ, ϵ_R/R, and ϵ_{P_c}/P_c are the relative errors of σ, R, and P_c, respectively; ϵ_σ, ϵ_R, and ϵ_{P_c} are the respective absolute errors. The drop radius, R, is calculated with Eq. [5], while the capillary pressure, P_c, of the water drop immersed in oil is given by the expression (cf. Eqs. [1], [5], and [6])

$$P_c = \frac{\partial P}{\partial U} (U - U_0) - \Delta \rho g \Delta z. \qquad [A.3]$$

Applying Eq. [A.1] to Eqs. [5] and [A.3], we obtain the following expressions for ϵ_R and ϵ_{P_c}:

$$\epsilon_R = \left\{ 0.25 \left[1 - \left(\frac{R_c}{H} \right)^2 \right]^2 \epsilon_H^2 + \left(\frac{R_c}{H} \right)^2 \epsilon_{R_c}^2 \right\}^{1/2} \qquad [A.4]$$

$$\epsilon_{P_c} = \left[(U - U_0)^2 \epsilon_{\partial P/\partial U}^2 + \left(\frac{\partial P}{\partial U} \right)^2 \epsilon_{U-U_0}^2 + (\Delta \rho g)^2 \epsilon_{\Delta z}^2 \right]^{1/2}. \qquad [A.5]$$

R_c/H is close to 1 in the proposed FFD technique, because the

shape of the drop is close to a hemisphere. For instance, R_c/H varied from 1 to 1.2 in our experiments. Hence, ϵ_R depends mainly on the error of R_c (see Eq. [A.4]). That is why we measured R_c very precisely with an accuracy of 1 μm before the experiments. Hence, the absolute error of R calculated by Eq. [A.4] at $R_c/H = 1.2$, $\epsilon_H = 6$ μm, $\epsilon_{R_c} = 1$ μm is smaller than 1.8 μm. Since $R \geq R_c$, the relative error of the drop radius, ϵ_R/R, does not exceed 0.27% in our experiments. $U - U_0$ varied from about 1 V to about 3.5 V in the experiments at the water/hexane interface, hence P_c was in the range from 450 dyn/cm^2 to about 1500 dyn/cm^2. Bearing this in mind, and knowing that $\epsilon_{\partial P/\partial U} = 1.4$ dyn cm^{-2} V^{-1}, $\epsilon_{U-U_0} = 0.2$ mV, $\epsilon_{\Delta z} = 25$ μm, $\Delta\rho = 0.34$ g/cm^3, Eq. [A.5] yields $\epsilon_{P_c} \leq 5$ dyn/cm^2. Hence, the relative error of P_c does not exceed 0.34% in these experiments. The same is valid for the relative error of P_c in the experiments at the solution/air interface.

Finally, after substitution of the relative errors of R and P_c calculated above in Eq. [A.2] we obtain $\epsilon_\sigma/\sigma = 0.43\%$.

APPENDIX B: COMPARISON BETWEEN THE FFD AND THE EXPANDED DROP TECHNIQUES WITH RESPECT TO THE DROP DEFORMATION CAUSED BY GRAVITY

Bond number, Bo, can serve as a measure for the influence of gravity on the drop shape. By definition, it reads

$$\text{Bo} = \frac{\Delta\rho g d^2}{\sigma},$$

where d is a typical dimension of the drop. Let us take the drop radius, R, as such a typical dimension and form the ratio

$$\frac{\text{Bo}_{ED}}{\text{Bo}_{FFD}} = \left(\frac{R_{ED}}{R_{FFD}}\right)^2, \qquad [B.1]$$

where subscripts ED and FFD denote the respective quantities in the expanded drop (ED) and the FFD techniques. Due to the way a fresh interface is created, the drop shape in the FFD technique proposed by us is close to a hemisphere; therefore, $R_{FFD} \approx R_c$. R_{ED} can be estimated taking into account the fact that the fresh interface in the ED technique is created by fast expansion of an almost hemispherical drop with an area A^* to a drop with much larger area A_0. The drop interface after expansion should be "fresher" the greater the ratio A_0/A^* is. For simplicity, let us consider the drop before and after expansion as a spherical segment. Hence, the drop radius is given by Eq. [5], whereas for the drop area before and after expansion is valid,

$$A^* = 2\pi R_c^2 \qquad [B.2a]$$

$$A_0 = 2\pi R_{ED} H_{ED}. \qquad [B.2b]$$

From Eqs. [5] and [B.2] one obtains

$$R_{ED} = R_c \frac{A_0}{A^*}\left(2\frac{A_0}{A^*} - 1\right)^{-1/2}. \qquad [B.3]$$

Finally, after substitution of Eq. [B.3] in Eq. [B.1] we obtain

$$\frac{\text{Bo}_{ED}}{\text{Bo}_{FFD}} \approx \frac{A_0/A^*}{2 - A^*/A_0}. \qquad [B.4]$$

To assure fresh interface A_0/A^* has to be large; hence its reciprocal in the denominator of Eq. [B.4] can be neglected. Thus Eq. [B.4] reduces to

$$\frac{\text{Bo}_{ED}}{\text{Bo}_{FFD}} \approx 0.5 \frac{A_0}{A^*}. \qquad [B.5]$$

According to Refs. (17, 27), A_0/A^* in experiments performed by the ED technique is typically in the range 20 to 50. Hence, in view of Eq. [B.5] the drop shape is 10 to 25 times less affected by gravity in the FFD technique compared to the ED technique.

ACKNOWLEDGMENTS

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