Surface Tension Determination with a Teflon Rod

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The rod-pull method originally described by Padday[4] has proven a useful technique for the determination of surface tension. However, as generally practiced, it requires that the sample wets well the bottom of the rod. A variation on this method is described in which a low surface energy substrate makes contact with the sample. A smooth-bottomed rod of Teflon is used, and the surface tension of nonwetting samples is determined by fitting an experimental force curve to a family of simulated curves. The use of a low surface energy substrate may be of some utility in the study of fragile interfacial films.

Introduction

Many different techniques have been described for the determination of surface tension.[1,2] Some commonly used methods are based on the vertical force exerted on a substrate (rod, plate, or ring) by the surface of interest. Examples include the Wilhelmy method,[3] which requires a vanishing contact angle, and the "rod-pull" method described by Padday et al.[4]

According to the rod-pull method, one determines the maximum suspended weight (MSW) of a meniscoid which is attached to the bottom of a stainless steel cylindrical rod. Together with the sample density, this MSW can be interpreted in terms of surface tension by reference to a set of equations.[4,5] The MSW is an equilibrium quantity and can be approached from above or below, since it occurs at a meniscoid height below the maximum height (where the sample detaches due to surface failure).

Here, we report a variation on the rod-pull method which allows the use of a low surface energy substrate. As generally practiced, the rod-pull method requires that a sample's MSW be recorded in order to determine its surface tension. Therefore, sufficient wetting of the rod bottom is required so that contact angle limitations do not cause the sample to detach before the meniscoid has reached the MSW. In contrast, we record the entire force curve produced as the meniscoid is gradually elevated above the sample surface, using this curve to determine the surface tension. For this reason, we do not need to record the MSW. Whereas the bottom of the stainless steel rod used by Padday is roughened to increase wettability,[4] we are free to use a low-energy substrate. Our rod is smooth bottomed and made of Teflon.

Experimental Section

Materials. FEP Teflon is tetrafluoroethylene−hexafluoropropylene copolymer, a form of Teflon which is thermoplastically moldable. PTFE Teflon is poly(tetrafluoroethylene), a commonly used machinable form of Teflon which is produced from powdered material by a pressing process. FEP Teflon stock was purchased from Berghof America, Inc. (Concord, CA). PTFE materials were machined in a facility maintained by the Cornell Laboratory of Atomic and Solid State Physics. Polonium foil was obtained from NRD, Inc. (Grand Island, NY). The components of the experimental apparatus (linear actuator, stepping motor, solid coupling and planetary gearhead) were obtained through Axis, Inc. (Lebanon, NJ). Teflon Oak Ridge tubes (Nalge Corp.), carbon tetrachloride, glycerol, ethylene glycol, and methanol (all certified ACS grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Hexane and hexadecane (both 99+%) were obtained from Aldrich Chemical Co. (Milwaukee, WI).

Force Curve Apparatus. The apparatus used for the collection of experimental force curves is diagrammed in Figure 1. The Teflon rod is suspended from the pan of a semi micro analytical balance (model ER-182A, A&D Engineering, Milpitas, CA), centered above the sample. The sample (4−5 mL at the bottom of a 50 mL Teflon Oak Ridge tube) rests on a platform which is mounted on a linear actuator (model KR3306C-300L-02462, THK Ltd). The actuator is connected to a microstepping motor (model SX57-83, Compumotor) via a solid coupling and planetary gearhead (model 23PL-0280, Applied Motion Products). The motor is driven by a control unit which is operated by a Macintosh computer. The computer is interfaced by RS232 connections, via modem and printer ports, to both the control unit and the balance. Data collection is automated, under the control of a dedicated program written in FutureBasic. The balance and sample are enclosed in a cabinet which rests on vibration-damping pads (Polymer Dynamics).

Teflon Rods. Teflon rods are produced from 2 mm diameter FEP Teflon stock which is softened in a heated air stream before being drawn out to a neck of <0.8 mm diameter. After cooling, the neck is cut with a razor and the thin end of the gradually tapering rod stock is passed through a 0.889 mm hole which has been drilled perpendicularly through a flat, 1.5 cm thick block of PTFE Teflon. This block serves to hold the FEP rod normal to the grinding and polishing surfaces. When the tapering rod stock is seated in the block, excess material is cut off at the block face. The Teflon is hardened by immersion in liquid nitrogen, and the rod bottom is carefully ground flat over a roughened stainless steel surface. The rod and block are then cleaned and recooled in liquid nitrogen, and the rod bottom is polished on a smooth stainless steel surface. To hold a FEP rod perpendicular to the sample surface, a barrel (5 mm diameter) is machined from PTFE. The FEP rod is centered on the barrel axis at one end and a stainless steel hanging hook is centered on the axis at the other end. To reduce static charge near the sample surface, a sleeve of polonium foil is attached to the barrel.

Two issues must be considered when evaluating rod-bottom diameters. FEP Teflon is deformable, so a micrometer cannot be used. In addition, the shape of our rods is slightly tapering. Therefore, we use the surface tension value of hexadecane (27.5 mN/m at 20 °C[6]) in order to determine the diameter of our Teflon rod bottoms. As discussed below, the MSW is a function of surface

(1) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; John Wiley & Sons: New York, 1988; Chapter IIA, section 17.
(2) Couper, A. *Physical Methods of Chemistry*, 2nd ed.; Rossiter, B. W., Baetzold, R. C., Eds.; Investigations of Surfaces and Interfaces-Part A.; Wiley-Interscience: New York, 1993; Vol IXA, p 1.
(3) Harkins, W. D.; Anderson, T. F. I. *J. Am. Chem. Soc.* **1937**, *59*, 2189.
(4) Padday, J. F.; Pitt, A. R.; Pashley, R. M. *J. Chem. Soc., Faraday Trans. 1* **1974**, *71*, 1919.
(5) Christian, S. D.; Slagle, A. R.; Tucker, E. E.; Scamehorn, J. F. *Langmuir* **1998**, *14*, 3126.

(6) *Thermodynamic Tables: Hydrocarbons*, vol. IV, Thermodynamic Research Center; Texas A&M University: College Station, TX, 1985; p e-1101.

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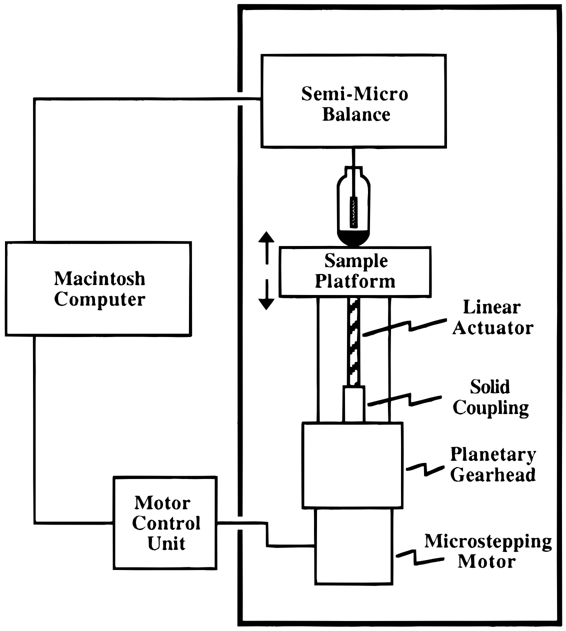

Figure 1. Apparatus for the collection of experimental force curves.

tension, density, and rod-bottom diameter. We measure the $MSW_{hexadecane}$ for a given rod and then find the rod-bottom diameter consistent with this value. These diameters are consistent with estimates based on microscopy.

Data Collection. The data collection procedure is as follows: the rod is rinsed in a series of clean solvents, dried by dabbing on a lint-free absorbent wipe, and carefully suspended from the bottom of the balance pan by a stainless steel extension wire. The chamber door is closed gently, and when the rod is still, the data collection program is initiated. The sample is raised until the bottom of the rod is 1−3 mm from the sample surface, and the program waits until the balance readout has stabilized. The balance is then tared, and the platform begins to move upward at 25 μm/s. As the rod contacts the surface, a force (either buoyant or wetting) registers on the balance. The program stops the platform and then begins to move it downward at 2.5 μm/s. As the sample moves downward, the program records paired data (sample weight and platform height) sent by the balance and control unit. The force curve is plotted to the computer screen as it develops. To verify the equilibrium form of a force curve, data can be collected as the sample platform rises or falls, and the platform can be stopped at any given height to demonstrate the stability of a suspended meniscoid mass. A force curve is collected until the sample breaks free, at which point the sample platform accelerates to 2.5 mm/s, clearing the sample well below the rod. Force curves are saved to disk as text files.

For a finite sample, the plane of zero hydrostatic pressure (against which meniscoid height must be measured) will fall as the volume of the elevated liquid increases. Of course, this effect can be neglected if the diameter of the sample vessel is suitably large. But given the internal diameter of the sample tubes we use (2.50 cm), our experimental force curves are subject to a small but detectable distortion. The data are easily corrected to account for this effect. Each experimental force curve is processed so that to each apparent meniscoid height (h_i) is added a correction proportional to the meniscoid mass (m_i): the meniscoid volume divided by the cross-sectional area of the sample vessel, $(m_i/\rho)/(\pi r_{tube}^2)$. Our rods are sufficiently small in diameter[7,8] ($d_{vessel}/d_{rod} > 28$) that wall effects do not perturb the experimental force curves.

Simulation of Force Curves. The model which we use to generate simulated force curves assumes no wetting of the Teflon rod. This model has been described by Padday et al.,[4] and sample

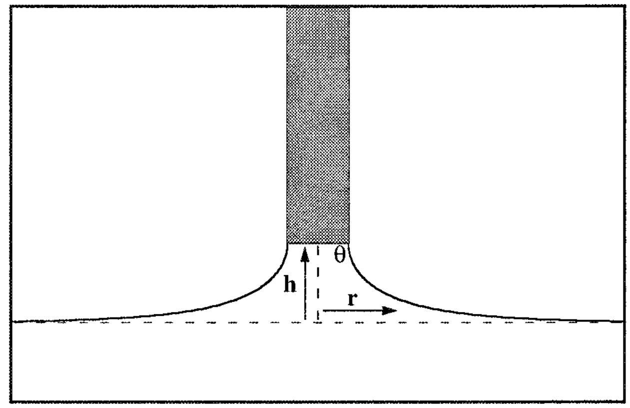

Figure 2. An axisymmetric meniscoid suspended from the bottom of a cylindrical rod. h is the height above the plane of zero hydrostatic pressure, r is the distance from the rod axis, and θ is the angle which a tangent to the meniscoid surface makes with the rod bottom at the three-phase boundary.

adhesion is to the bottom of the rod only, as shown in Figure 2. As the sample is lowered away from the rod, the suspended meniscoid increases in mass, producing a force curve. At any given meniscoid height, h_o, the meniscoid volume is determined by four parameters only: the gravitational constant, g; the density difference between sample and air, ρ; the rod-bottom radius, r_o; and the surface tension, γ.[4] To generate a force curve, the simulation program fixes these parameters and then steps through a sequence of increasing meniscoid heights. At each h_o, the shape of the suspended meniscoid is obtained by numerical integration of the Young−Laplace equation[4]

$$(\mathrm{d}^2h/\mathrm{d}r^2)/[1 + (\mathrm{d}h/\mathrm{d}r)^2]^{3/2} + q(\sin\theta/r = h/q \qquad (1)$$

where q is the meniscus coefficient, $q = (\gamma/\rho g)^{1/2}$. The density of air was taken to be 0.001 g/mL.[9] Nominal liquid densities were verified by weighing precisely determined volumes of each liquid. The integration program was written in C and runs on a Power Macintosh 7200/120 computer. A typical force curve of 100 data points can be generated in 3 h. The output is equivalent to the information published in tabular form by Padday,[4,10] as demonstrated in Figure 3.

Interpretation of Experimental Force Curves. Two different strategies can be used to obtain the surface tension value implied by an experimental force curve, depending on whether the sample wets the Teflon rod. If the sample is nonwetting, than a "best fit" is sought to the entire, experimentally accessible portion of the force curve. This fit is drawn from a family of simulated curves, corresponding to different surface tensions, for the appropriate rod-bottom diameter and sample density. If the sample is wetting, then a fit can still be done to the portion of the experimental curve which exceeds the wetting height. However, since such samples yield an MSW, it is easier to relate this to a surface tension in the manner described by Padday et al.[4] A curve relating MSW to surface tension can be prepared by simulation, as well.

Results

A comparison of experimental and simulated force curves for three nonwetting liquids is shown in Figure 4A. The surface tension estimates derived from these fits compare well with the literature values (Table 1). The glycerol and ethylene glycol samples break free from the rod due to contact angle limitation (see Discussion).

(7) Furlong, D. N.; Hartland, S. *J. Chem. Soc., Faraday Trans. 1*, **1980**, *76*, 457.
(8) Furlong, D. N.; Hartland, S. *J. Chem. Soc. Faraday Trans. 1*, **1980**, *76*, 467.

(9) *CRC Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1982.
(10) Padday, J. F. Tables of the Profiles of Axisymmetric Menisci (published as a set of microfiches); *J. Electroanal. Interfacial Electrochem.* **1972**, *37*, 313.
(11) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; John Wiley & Sons: New York, 1988; Chapter IIA, section 1.

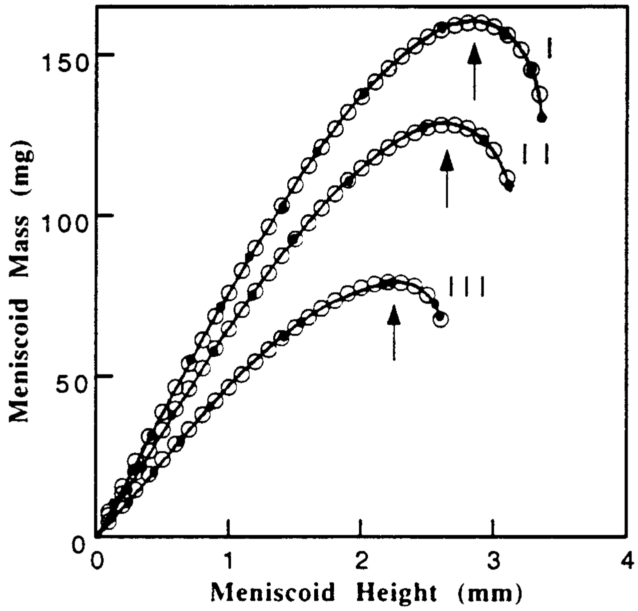

Figure 3. Comparison of simulated force curves (○) and those constructed from the tabulated data of Padday (●). Curves represent a meniscoid of water ($\gamma = 72.5$ mN/m, $\rho = 0.998$ g/mL) elevated by three rods of different diameter: 4.7834 mm (I), 4.0784 mm (II), and 2.8330 mm (III) (see ref 4). For each curve, the maximum suspended weight (MSW) is indicated by an arrow.

Table 1. Experimentally Determined Surface Tensions Compared with Literature Values[a]

sample	literature surface tension (mN/m)	experimental surface tension FEP rod (mN/m)
glycerol	63.3	63.1 ± 0.2
ethylene glycol	46.5	46.7 ± 0.1
methanol/water (1:1 v/v)	35.3[9]	35.4 ± 0.1
carbon tetrachloride	26.4[(25 °C)]	26.6 ± 0.1
methanol	22.5	22.4 ± 0.1
hexane	18.4	18.3 ± 0.1

[a] Experimental force curves were collected between 22 and 24 °C and results are expressed as the average of five replicate samples, together with the range of values observed. Unless otherwise indicated, literature values are taken from ref 11 and are for 20 °C.

However, the methanol/water (1:1 v/v) sample reaches the MSW before detachment (Figure 4A, curve III).

Experimental and simulated force curves for three wetting liquids are shown in Figure 4B. These simulated curves do not merge with the experimental curves until the meniscoid height has exceeded the wetting height. However, above this height the simulated and experimental curves coincide, yielding a MSW for each sample. The surface tension estimates based on these MSWs agree with the literature values (Table 1).

Discussion

Consider first the force curves shown in Figure 4A. While the MSW does occur before the maximum meniscoid height, it is not realized until θ (Figure 2) goes below 90°.[4,10] Of course, $\theta < 90°$ is not a stable condition for nonwetting liquids, and these samples generally detach from the Teflon rod because θ has dropped below their receding contact angle, φ_r. For example, glycerol and ethylene glycol break free of the rod well before the MSW (Figure 4A, curves I and II). Indeed, it is generally true that nonwetting samples break free due to contact angle limitation ($\theta < \varphi_r$) before reaching the MSW. An exception

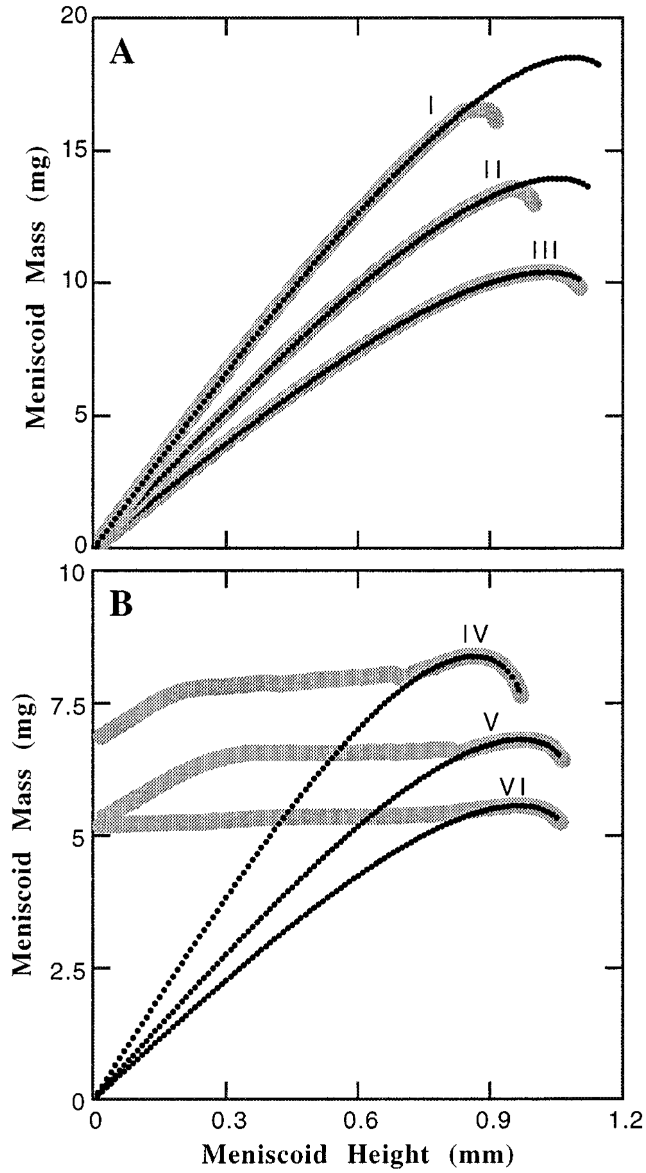

Figure 4. Comparison of experimental and simulated force curves. For each liquid, the experimental force curve (gray area) is shown together with the simulated curve (···), which corresponds to the best-fit estimate of surface tension. (A) Nonwetting liquids: glycerol (I), ethylene glycol (II), and methanol/water (1:1 v/v) (III). (B) Wetting liquids: carbon tetrachloride (IV), methanol (V), and hexane (VI).

to this rule is methanol/water (1:1 v/v). Despite its rather low surface tension, this liquid mixture does not appear to wet FEP Teflon, so its advancing contact angle, φ_a, must be greater than 90°. But this liquid remains stably attached to the rod until just after the MSW (Figure 4A, curve III), so φ_r must be less than 90°. It need not be much less, though. Because our FEP rods are of fairly small diameter (<0.9 mm), θ_{MSW} is near 90° for most liquids.[4,10]

For liquids which wet Teflon, φ_a is already less than 90° and φ_r is smaller still. For this reason, wetting samples remain stably attached to the rod bottom and their force curves pass through the MSW. Because these samples wet the side of the Teflon rod, the experimental and simulated force curves coincide only above the wetting height, though agreement between the curves is quite good in this regime.

Regardless of whether a sample wets Teflon, the same strategy can be employed to determine its surface tension from the experimental force curve: seek a best fit between simulated and experimental curves over the appropriate range of meniscoid heights. For nonwetting samples, this is usually the only available strategy and it is quite successful. However, for wetting samples it is also possible, and probably easier, to use the MSW as proposed by Padday.[4] Both strategies produce equivalent results.

It is often noted that the conventional rod-pull method is independent of contact angle considerations,[1,5] but this is only true if the sample does not detach from the rod prior to reaching the MSW.[4,5] In other words, the rod-pull method is indirectly dependent on contact angle, insofar as it requires that $\varphi_r > \theta_{MSW}$. The variation we have described, based on force curve analysis, requires only that $\varphi_r < 180°$.

The principal distinction of the method we have described is the use of a low surface energy substrate: a smooth-bottomed Teflon rod. It may be the case that a low surface energy substrate will offer advantages for the study of interfacial films which are slow to equilibrate. Such systems may be perturbed by contact with a high-energy substrate, and we are currently conducting studies to determine the extent of any such effect.

Acknowledgment. The authors thank Dr. Sheldon Wesson for guidance in assembling the force curve apparatus. J.T.B. was supported by National Institutes of Health Research Service Award I-T32-GM08267. J.H. was supported by the W. M. Keck Foundation. This work was supported by National Science Foundation Grant MCB-9722818.

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