

Surface Films of Soybean Lecithin I

Development of a Recording Film Balance

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In the course of a study of the surface properties of soybean lecithin, a modification of the Wilhelmy or vertical-type film balance was developed which is believed to offer certain advantages over other standard film balances. The apparatus, which employed a displacement-type transducer as the sensing device, was found to be a reliable sensitive instrument. Its principal advantage was the fact that a recorder could be operated conveniently off the transducer element.

IF THE surface tension of a liquid is lowered by the addition of a solute, then, as predicted by the Gibbs equation, the solute must be adsorbed at the surface or interface. This adsorption may be sufficient to produce a monomolecular layer or film of solute molecules on the surface. The monolayer is considered to exert a film pressure, π , which may be defined as

$$\pi = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$$

where γ_{solvent} is the surface tension of the film-covered solution. Theoretically, any method capable of measuring surface tension allows the calculation of the film pressure. In practice, however, only two different types of instruments are in common use, the Langmuir type or horizontal film balance and the Wilhelmy or vertical-plate film balance.

A modern horizontal film balance consists of a rectangular trough with a moving barrier that compresses the surface film against a fixed floating barrier. What is measured is the difference in surface tension between the liquids on either side of the floating barrier (1). The difference between the two surface tensions is, by definition, the film pressure.

Basically, the Wilhelmy balance consists of an immersion plate, usually glass or platinum, which is attached to the arm of a balance. The plate is partially immersed in the film-covered subsolution. When the plate is partially immersed in a liquid, there is a downward pull on the plate which is directly proportional to the surface tension. If a film is layered on the liquid, the surface tension is reduced, and the plate will rise until buoyancy compensation is reached. For the measurement of the surface pressure of insoluble films with this apparatus, it is necessary

to construct a film trough for compression of the film.

DESIGN OF APPARATUS

The objective of this investigation was to improve the standard Wilhelmy film balance by providing a convenient means of recording the changes in surface pressure produced by compression of an insoluble monolayer. The modification employed involved the use of a displacement-type transducer element as a sensing device instead of the customary analytical balance. Figure 1 depicts the general appearance of the transducer element and other apparatus components as they were employed in the film balance. This photograph also shows the film trough which was constructed for use in conjunction with the transducer sensing device.

The output of the transducer was read directly off the meter of a d.c. amplifier or obtained from the tracing of the recorder which was operated off the amplifier.

Materials and Equipment.—The two transducers which were evaluated in this study were model G7A-0.15-350 and G7A-0.30-350 unbonded displacement transducers, manufactured by the Statham Instrument Co., Los Angeles, Calif. Both transducers had a bridge resistance of approximately 350 ohms and required applied forces of approximately 0.15 and 0.30 oz., respectively, to produce a maximum probe displacement of ± 0.015 in.

The d.c. amplifier used was a Hewlett-Packard model 425A microvolt ammeter. The voltage range of this instrument was from 10 μ v. end scale to 1 v. end scale. The recorder employed was a model G-11A Varian Graphic Recorder.

Construction of Sensing Device.—Figure 2 shows the diagram of the external circuit used to connect the transducer to the power supply and d.c. ampli-

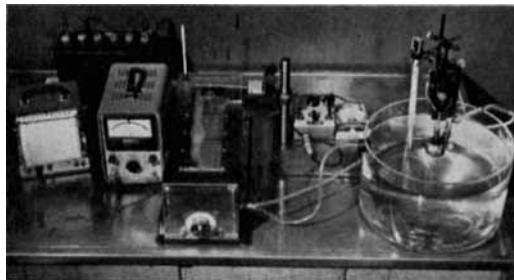


Fig. 1.—Apparatus (trough covered).

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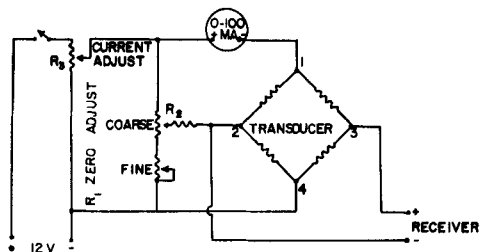


Fig. 2.—External circuit diagram. Key: transducer terminals 1 and 4, power input; transducer terminals 2 and 3, output to receiving instrument; R_1 , 1000- and 25000-ohm wire-wound potentiometers; R_2 , 25000-ohm wire-wound resistor; R_3 , 100-ohm 5-w. wire-wound potentiometer.

fier. The circuit employed used a 100-ohm 5-w. potentiometer as a voltage divider, whereby the input current from a 12-v. storage battery was maintained at a fixed value as indicated on a milliammeter. Two 2-w. wire-wound potentiometers of resistance 25,000 and 1000 ohms were wired in series to provide a coarse and fine adjustment for balancing the bridge.

To increase the sensitivity of the transducer, an aluminum extension arm was attached to the transducer probe. The length of the extension arm was 11.5 cm. The immersion plate was suspended from the tip of the extension by a length of small-diameter aluminum tubing to which a small hook and ring had been attached at opposite ends. The transducer itself was mounted on an adjustable rack which in turn was supported by a heavy brass base equipped with leveling screws.

The aluminum extension arm for the transducer probe was hand-shaped from $\frac{1}{8}$ -in. aluminum rod. The arm was flattened on two sides tapering gradually to the tip. The bottom edge also was tapered to a lesser extent, and a small notch was made on the upper edge of the tip to accommodate the immersion plate-hook assembly. The butt of the extension arm was flattened slightly on both sides normal to the taper for a distance of approximately $\frac{3}{16}$ in. A hole $\frac{2}{64}$ in. in diameter was tapped through the center for attachment to the probe of the transducer. A nylon screw was used to make the attachment.

The immersion plate was attached to the end of the aluminum arm by a 6-cm. length of aluminum tubing (outer diameter 1 mm.) to which a small platinum hook and ring were affixed at opposite ends with epoxy resin cement.

The weight of the entire arm assembly attached to the transducer probe was 0.828 Gm. The weight of the aluminum arm itself, including the nylon screw, was 0.793 Gm.

The immersion plates were constructed from Corning microscope cover glasses. The dimensions of these cover glasses were 15×50 mm. The thickness was 0.14 to 0.15 mm. A sand blaster equipped with a fine abrasive and a small tip was used to perforate the cover glasses in the center of one of the 15-mm. sides about 3 mm. from the edge and to depolish their entire surfaces. The perimeter of each glass immersion plate was measured with a vernier gauge, and each plate was stored prior to use in an individual labeled container.

Construction of Film Trough.—The film trough was constructed of 0.25-in. stainless steel plates which were welded together and then milled so the upper surface was perfectly flat. The upper inner walls of the trough were also carefully milled to provide a rectangular enclosure of known dimensions. The inner dimensions were found by measurement to be 9.99 by 39.32 cm. The trough was provided with a hollow chamber beneath the upper reservoir through which water from a constant-temperature bath was circulated. One end of the trough had a well designed to accommodate the immersion plate of the apparatus. The threaded rod, which moved the moving barrier of the trough, was made to extend beyond the cover for the trough, thus providing for external manipulation of the trough when covered. The threaded drive rod was carefully machined from brass. The barrier yoke was found to traverse a distance of 0.508 cm. per complete revolution of the drive rod. The fixed barrier of the trough was adjustable and was aligned parallel to the moving barrier used to compress the film.

A cover constructed of 24-gauge stainless steel and Plexiglas was constructed to fit closely over the top of the trough. The drive rod extended through a Teflon seal in one end which allowed the drive rod to turn freely but was also reasonably air-tight. A circular hole was made in the Plexiglas top of the cover at one end to allow passage of the immersion plate. A disk of Plexiglas with an opening approximately 4 mm. in diameter in its center was used to seal the larger opening. The length of aluminum tubing used to attach the immersion plate to the extension arm of the probe passed through the small opening in the disk.

Additional openings in the cover were provided for sample introduction, the placing of a thermometer, and hoses for circulation of water through the hollow chamber in the trough. The sample introduction opening was covered during the course of a determination.

The cover itself bolted down on a Neoprene rubber

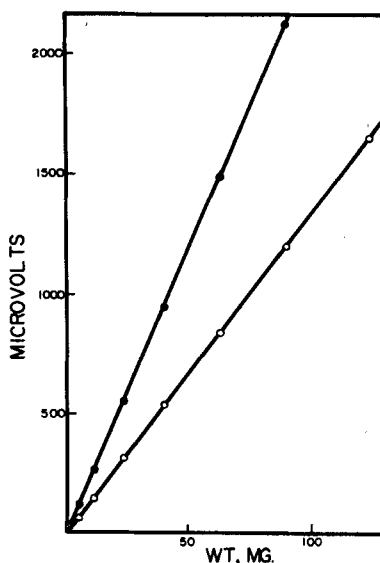


Fig. 3.—Calibration plots for Statham model G7A-0.15-350 (●) and G7A-0.30-350 (○) transducers.

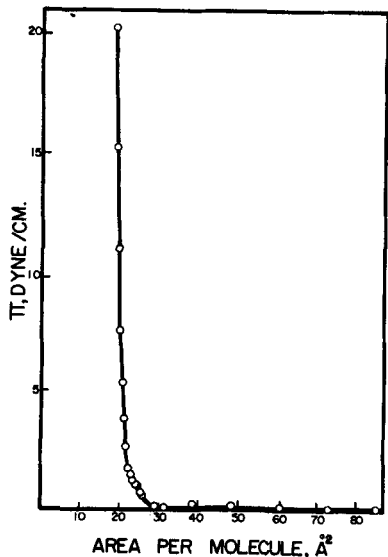


Fig. 4.—Palmitic acid isotherm determined by compression with film trough (23.5°C.).

covered steel base to give a tight fit. Water from a constant-temperature bath was circulated through the hollow chamber of the film trough.

EXPERIMENTAL

Reagents and Materials.—Triple-distilled reagent grade benzene was used as the spreading solvent for the sample solutions. The water used in the subsolutions was prepared by passing distilled water through a mixed bed ion exchange column and then redistilling the deionized water. The paraffin (m.p. 65–70°) used to coat the film trough was melted and extracted several times with hot ethanol. The high-purity palmitic acid (m.p. 63.5°) used in the compression experiments was supplied by Mann Research Laboratories, New York, N. Y.

The sample solutions were delivered to the surfaces of the subsolutions in volumes ranging from 0.010 to 0.100 ml. Calibrated micropipets were normally used to deliver the solutions for the compression experiments with the film trough, although a 0.100-ml. capacity Hamilton microliter syringe with a Chaney adaption also was used with equal success in some of the experiments.

Calibration of Apparatus.—The apparatus was calibrated by suspending small platinum weights from the end of the aluminum extension arm and noting the meter deflection produced. It was necessary to determine whether the change in buoyancy of the immersion plate as it rose out of the liquid contributed significantly to the electrical output of the transducer. An analysis of the force-displacement characteristics of the two model G7A transducers used in the study indicated that the error introduced by buoyancy effects would be negligible. This conclusion was checked experimentally by attaching an immersion plate to the end of the aluminum arm, partially immersing the plate in water, and then adding the calibration weights to the arm. The calibration plot remained linear and had the same slope as calibration plots obtained in the usual manner.

A comparison of the relative sensitivities of the two transducer units may be obtained by inspection of the plot shown in Fig. 3. The G7A-0.15-350 transducer was approximately 1.8 times as sensitive as the G7A-0.30-350 transducer and was employed for the majority of the experiments. The plot also shows that the electrical output of the apparatus was directly proportional to the force applied at the end of the probe.

The relationship between the transducer output and the surface pressure was calculated from the calibration data. This was done by multiplying the applied weight by the acceleration due to gravity, thereby obtaining the force in dynes which produced a certain observed electrical output. Dividing this force by the electrical output in microvolts gave the number of dynes per microvolt.

For example, from the calibration data obtained for the G7A-0.15-350 transducer, the calibration factor for the relationship between applied force and electrical output was calculated to be 0.0412 dyne/ μ v. The surface pressure for any given measurement was then calculated from the relationship:

$$(\text{dyne/cm.}) = \frac{(0.0412 \text{ dyne}/\mu\text{v.})(\text{output}, \mu\text{v.})}{(\text{immersion plate perimeter}, \text{cm.})}$$

The sensitivity of the film balance was limited by the stability of the signal obtained from the d.c. amplifier. The amplifier noise was estimated to be approximately 1 μ v. The drift was found to be a maximum of 2.4 μ v. over a 2-hr. period. The error due to drift during this time period can be calculated in terms of its effect on the film pressure using the calibration data for the G7A-0.15-350 transducer

$$\pm \pi = \frac{(0.0412 \text{ dyne}/\mu\text{v.})(2.4 \mu\text{v.})}{(\text{immersion plate perimeter}, \text{cm.})}$$

Thus, the error would be within ± 0.03 dyne/cm. for an immersion plate with a perimeter of 3.0 cm.

Surface Tension Measurements.—As a check on the accuracy of the apparatus, the surface tensions of distilled water and triple-distilled benzene were determined at room temperature (23.0°). The measurements were obtained by balancing the bridge with the immersion plate suspended above the surface of the liquid. The plate was then lowered until the bottom edge touched the surface. The plate was then detached from the surface by slowly raising the plate. The maximum output of the transducer at detachment from the surface was directly proportional to the surface tension. The values obtained were 72.3 dynes/cm. for water and 28.5 dynes/cm. for benzene. These values compared favorably with those given in the "International Critical Tables" (2) of 72.28 ± 0.05 dynes/cm. for water at 23° and 28.88 ± 0.03 dynes/cm. for benzene at 20°.¹

Films of Palmitic Acid.—The compression isotherm for palmitic acid at 23.5° shown in Fig. 4 was obtained by rapid compression of the film at low values and then slow compression at 2-min. time intervals during the steep portion of the isotherm. The tracing of the compression isotherm obtained with the recorder clearly indicated the values observed during the steep portion of the isotherm were

¹ Calculated value for benzene at 23°: $\gamma(\text{air}) = 31.58 - 0.137t + 0.00001t^2 \pm 0.2 = 28.48 \pm 0.2$ dynes/cm.

not equilibrium values. The compression was carried out over a total time of 1.5 hr. The sub-solution was freshly redistilled deionized water. The limiting area for the monolayer, obtained by extrapolation, was approximately 21 \AA^2 per molecule.

The isotherm obtained for palmitic acid was very similar to that reported by Harkins (3) for palmitic acid at comparable temperatures. The recordings obtained for a number of compression isotherms for palmitic acid indicated that equilibrium was approached very slowly at high film pressures for this substance. Palmitic acid was observed to exhibit sharp decreases in film pressure following a small reduction in surface area per molecule. This initial rapid fall in film pressure was of short duration, ordinarily less than 2 min., and was followed by a slow equilibration of much longer duration. As the time required for complete equilibration films would have been prohibitively long, the films were compressed at regular time intervals as indicated by the recorder.

DISCUSSION

The analysis of the force-displacement characteristics of the Statham G7A transducers and the calibration data obtained for these elements indicated that a suitable sensing device for a recording film balance could be assembled from these components. The results of surface tension measurements and the reproduction of standard isotherms for palmitic acid strongly supported the view that the data obtained with the apparatus was comparable with that obtained with other conventional film balances.

While the use of a transducer element as the sensing device for a film balance is not a radical departure from a conventional Wilhelmy-type apparatus, it does offer certain substantial advantages. The principal advantage of the apparatus is that a recorder may be conveniently operated with the film balance. Other investigators have previously devised film balances with some sort of recording device. These recording devices have included complicated photographic techniques (4) or mechanical contrivances such as the use of a kymograph (5). Apart from the fact that the use of a recorder

provides a convenient and permanent record of each compression isotherm, there are other advantages which dictate the use of a recorder if possible. The use of a recorder is particularly advantageous for surface tension measurements by the detachment method. The visual determination of the maximum displacement obtained at the instant of detachment of the liquid surface from the immersion plate is less reliable and reproducible than obtaining the maximum value conveniently from a tracing of the detachment process.

The use of a recorder also allows the operator of the film balance to estimate the rapidity with which equilibrium is reached during the compression of the film. Another advantage is that the present apparatus could be easily modified to provide automatic recording of the compression isotherm as the film is compressed slowly over a period of hours by means of a motor connected to the drive rod of the film trough.

While the error due to meter drift over a 2-hr. period was estimated to be approximately ± 0.03 dyne/cm. for an immersion plate of perimeter 3.0 cm., the instantaneous error due to meter noise in the apparatus would be less than one-half this value. While this represents a satisfactory degree of sensitivity for most film pressure measurements, the sensitivity could be increased appreciably by the use of larger immersion plates. Recently, extremely sensitive semiconductor strain gauges have been developed and are commercially available (6). It is likely that it would be possible to design a film balance with many times the sensitivity of the present apparatus using a semiconductor strain gauge as the sensing device. The use of a more sensitive detection device would necessarily have to be accompanied by similar improvements in temperature control of the apparatus.

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