189. *A Torsion Microbalance for Measuring Low Pressures of Monolayers.*

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A description of the apparatus and technique for measuring low surface pressures of monolayers is given. A fibre loop on the surface of a liquid contains a reference monolayer, and the monolayer to be studied is spread outside. If the ring is held at one end of a diameter and pulled at the other, the fibre forms two arcs of a circle. The difference of pressure within and outside the loop is measured by the tension required for extension. In the apparatus the tension required is measured by a torsion wire.

Apparatus for measuring low pressures of monolayers are generally of two types: the hanging-plate type and the surface-balance type. The former, introduced by Dervichian (*J. Phys. Radium*, 1935, **6**, 221, 429) and Harkins and Anderson (*J. Amer. Chem. Soc.*, 1937, **59**, 2189), was used by Bull (*ibid.*, 1945, **67**, 4, 5) for measuring the surface pressure of protein films. The method is simple and, when properly used, reliable. It requires, however, precise temperature control and a careful choice of material for the hanging plate, since a small change of wetting angle owing to the deposition of a monolayer may introduce large errors.

These apparatus have in common the division of the liquid surface into two parts: the substance to be studied is spread on one part, while the other part is kept at a constant surface pressure, usually as low as possible. The difference in pressure between the two parts is compensated for by means of a known force. In apparatus of the Langmuir type, adapted for measuring small surface pressures by Adam and Jessop (*Proc. Roy. Soc.*, 1926, *A*, **110**, 423) and slightly improved by Harkins (see Weiseberger, "Physical Methods of Organic Chemistry," Interscience Publishers, N.Y., 1945), these two parts are divided by a mica barrier and thin threads covered with vaseline. The necessity of keeping the water level constant makes satisfactory cleaning of the surface impossible in this type of apparatus, and it is also difficult to prevent leakage at the connections between the floating barrier and the threads.

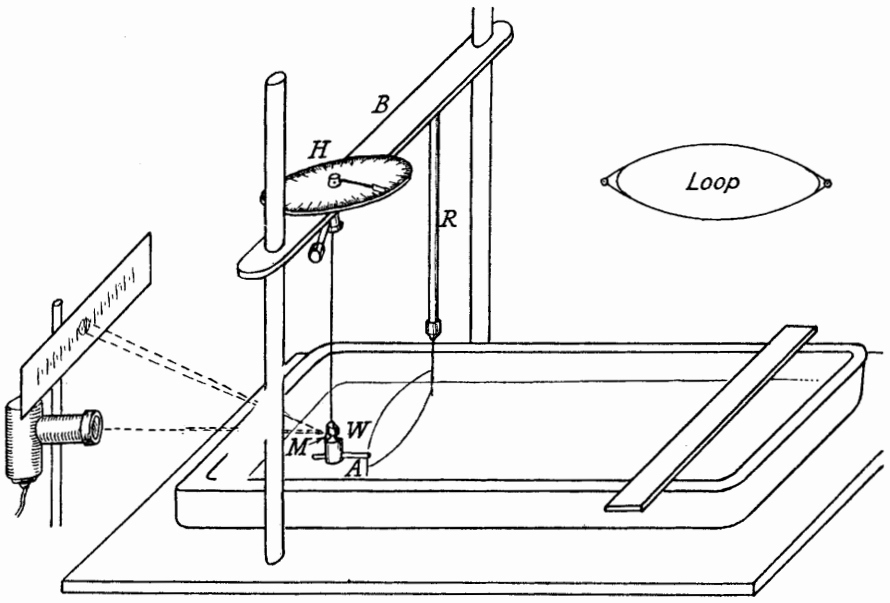
The most sensitive apparatus, developed by Guastalla (*Cahier de Physique*, 1942, **10**, 36), enables pressures of the order of millidynes/cm. to be measured. The two parts of the surface are separated by a vaselined thread which is kept in tension by an arm attached to a weight hung on a torsion wire. The pressure difference forces the thread into the arc of a circle. As long as the displacement of the thread is small, it is proportional to the pressure difference, at constant tension; or, for a constant displacement, the pressure difference is proportional to the tension. Disadvantages of this method are the possibility of leakage at the solid–thread connections and the relatively complicated optical system necessary to obtain sufficient accuracy. The necessity of keeping the level constant was avoided by the introduction of a

floating frame. It is, however, regrettable that a more complete description of experimental details has not been published.

As none of the above methods was entirely satisfactory for measuring surface pressures of the order of 10^{-3} dyne/cm., a new method has been developed.

Principle of the Method.—A thread is tied in a closed loop and placed on the surface of the water; when this is done properly there is no leakage between monolayers inside and outside the loop. If the film inside has the greater surface pressure the loop becomes circular so as to enclose the maximum area. If one point of the loop is fixed and the point opposite is pulled, the loop is forced into the form of two arcs of a circle, again enclosing the maximum area possible. The tension is applied to the loop by means of an arm attached to the weight W, hung on a torsion wire (Fig. 1). When this arm is kept in a fixed position the tension is proportional to

FIG. 1.



the angular displacement of the torsion head. Thus the force required to keep the loop at a constant length can be measured by the torsion required to keep the position of the weight as indicated by the light spot, and hence the difference in pressure can be calculated. During the experiment it is necessary to have a monolayer inside the loop whose surface pressure is constant, greater than that of the outside monolayer to be studied.

Derivation of Fundamental Relations.—For the loop formed by two arcs of a circle according to Fig. 2, we have

$$l = R\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$a = R \sin \frac{\phi}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The relation between the surface pressure π and the force f can be calculated from the condition that the work necessary to expand the loop is equal to the work necessary to compress the film; *i.e.*,

$$-\pi . \, dA = 2f . \, da \text{ or } \pi = -2f/(dA/da) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is the area enclosed by the loop, so that

$$\tfrac{1}{2}A = \tfrac{1}{2}\phi R^2 - aR \cos \frac{\phi}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Substituting from equations (1) and (2), we obtain

$$\tfrac{1}{2}A = \tfrac{1}{2}lR - a(R^2 - a^2)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

and after differentiation and rearrangement

$$\tfrac{1}{2}(dA/da) = (dR/da)[\tfrac{1}{2}l - aR(R^2 - a^2)^{-\frac{1}{2}}] + (R^2 - a^2)^{-\frac{1}{2}}(2a^2 - R^2) \quad . \quad . \quad (5)$$

From equation (1), since l is constant, we have

$$d\phi/da = -(\phi/R)(dR/da) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and from equation (2)

$$1 = \sin\frac{\phi}{2}\cdot\frac{dR}{da} + \frac{1}{2}R\cos\frac{\phi}{2}\cdot\frac{d\phi}{da} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Substituting for $d\phi/da$ from equation (6) in equation (7), we get

$$1 = \sin\frac{\phi}{2}\cdot\frac{dR}{da} - \frac{1}{2}\phi\cos\frac{\phi}{2}\cdot\frac{dR}{da}$$

which, on elimination of ϕ and rearrangement, gives

$$1 = \frac{1}{R^2}(R^2 - a^2)^{\frac{1}{2}}[aR(R^2 - a^2)^{-\frac{1}{2}} - \tfrac{1}{2}l]\frac{dR}{da}$$

or

$$(dR/da)[\tfrac{1}{2}l - aR(R^2 - a^2)^{\frac{1}{2}}] = -R^2(R^2 - a^2)^{-\frac{1}{2}}$$

FIG. 2.

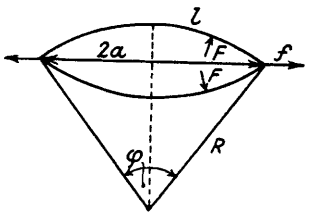
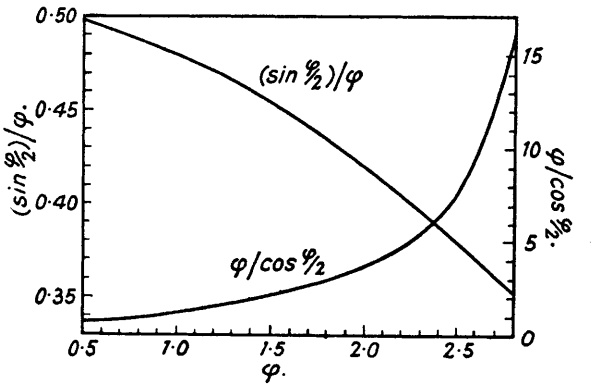


FIG. 3.



Substituting in equation (5), we then have

$$\tfrac{1}{2}(dA/da) = -R^2(R^2 - a^2)^{-\frac{1}{2}} + (R^2 - a^2)^{-\frac{1}{2}}(2a^2 - R^2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and by rearrangement

$$dA/da = 4(R^2 - a^2)^{\frac{1}{2}}$$

which, introduced into equation (3), gives

$$\pi = \tfrac{1}{2}f(R^2 - a^2)^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Substitution of $(R^2 - a^2)^{-\frac{1}{2}} = (\phi/l)/\cos\frac{\phi}{2}$ from equations (1) and (2) gives the final relation between the pressure of the film inside the loop and the force applied to the loop, *viz.* :

$$\pi = (f\phi/2l)/\cos\frac{\phi}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

In practice, $(\sin\frac{\phi}{2}/\phi)$ is calculated from the known values of a and l, and the value of $\phi/\cos\frac{\phi}{2}$ is obtained for the same value of ϕ from the graph (Fig. 3).

The area enclosed by the loop may be calculated from equation (4*b*), which may be written as

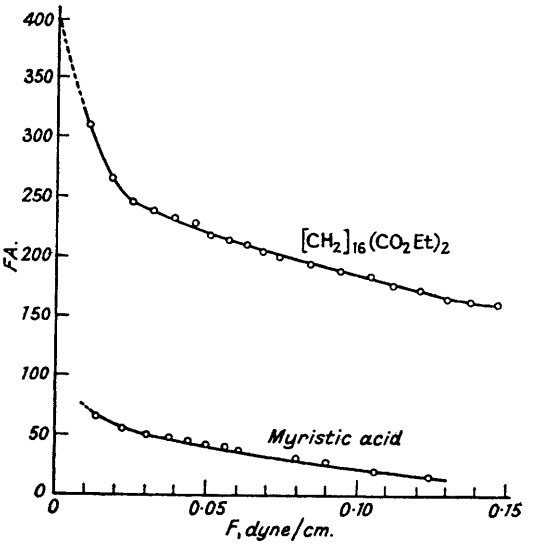
$$A = \frac{l^2}{\phi} - 2al\frac{\cos\frac{\phi}{2}}{\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4c)$$

Equation (9*a*) shows that the highest sensitivity is obtained for small values of $\phi/\left(\cos\frac{\phi}{2}\right)$, which are obtained with an elongated loop. Work in this region, on the other hand, suffers from the disadvantage that a small change of the length corresponds to a big change in the area

enclosed by the loop. This substantially changes the pressure of the film inside the loop which decreases the sensitivity of the adjustment of the constant length of the loop. In the apparatus described, the angle ϕ was approximately 1·5 radians, corresponding to a value of approximately 2 for $\phi/\cos\frac{\phi}{2}$.

An important factor in determining the sensitivity of the apparatus is the choice of the substance to be spread inside the loop. As mentioned above, the pressure inside the loop should change as little as possible with change of area. This limits the choice of material to those giving a gaseous or expanded film at pressures of 0·2—0·3 dyne/cm. Ethyl hexadecane-1 : 16-dicarboxylate was found to be satisfactory for this purpose. The sensitivity of the apparatus described (3×10^{-3} dynes/cm./div.) was found to be within the experimental errors of the rest of the experiment, *viz.*, cleaning the air, water, and solvent, and measurement of the volume of solution injected.

FIG. 4.



EXPERIMENTAL.

Description of the Apparatus.—The balance is shown diagrammatically in Fig. 1. The horizontal brass bar (*B*), which carries the torsion head (*H*) and the brass rod (*R*) supporting one end of the loop, is fixed to the top of the box in which the trough is contained. The rod *R* may be moved in the horizontal plane so that the loop can be adjusted to the desired length. The torsion head is divided into 180 divisions so that each division is equal to 2°. The concave mirror (*M*) and a horizontal arm (*A*), which is of adjustable length and holds the pin supporting the movable end of the loop, are attached to the torsion weight (*W*).

The loop is made of nylon thread, approximately 0·01 mm. thick, but, *e.g.*, terelin or polythene could be used, provided the thread is thin and strong enough.

Experience showed that to prevent leakage there must be no knots or crossings of fibres in the loop, and the fibre must be sufficiently hydrophobic. To ensure that the two arcs of the loop are equal, the loop was made from two fibres of equal length connected to two small circles of polythene with the hole for the needle in the middle (Fig. 1, inset). To prevent leakage at the fibre–polythene connections, these were protected by means of another fibre which was stuck to those forming the loop.

As the surface of nylon was not sufficiently hydrophobic, it had to be covered with the thin layer of a strongly hydrophobic substance. Vaseline, which is recommended by many authors, was found to be unsatisfactory because it spreads slightly itself and because it does not stick to the surface of the fibre very well. The best results were obtained with Everet's Vacuum Wax (No. 2, soft 60°). A thin layer of wax is put on the thread by means of a hot rod covered in molten wax. As temperature changes and contact with water cause the fibre to shrink, it is necessary to wet the fibre which is to be used for making the loop repeatedly with the molten wax to shrink it beforehand. For precise measurements it is still necessary to measure the total length from time to time and to allow for any alteration.

The air in the box, which enclosed the trough, was pumped out with the same water pump that was used for cleaning the surface, purified by bubbling through a column of dilute potassium hydroxide and water, and blown back into the box. The solution of the substance to be spread was injected on the water surface from an " Agla " microsyringe with a long thin needle which was inserted through a sheet of rubber covering a small window in the front of the box.

Calibration.—The torsion wire was calibrated by the swinging method. When the wire is twisted

through 2° the force f at the end of the torsion arm is given by $f = \pi^3 I/90\ t^2 d$, where I is the moment of inertia of the torsion arm and weight, d the length of the torsion arm, and t the period of swing. The moment of inertia of the torsion arm and weight was found by determining the period of swing of the torsion weight with the period of swing of another torsion weight the moment of inertia of which it was possible to compute. Then $I/I_0 = t^2/t_0^2$, where I_0 is the moment of inertia of a torsion weight used for calibration and t_0 is its period of swing.

In the apparatus described, the moment of inertia of the torsion weight I was 6·16 g.-cm.^{2} when the arm was adjusted to a length of 3 cm. The total weight was 18 g. The torsional force at the end of the arm was $5{\cdot}18 \times 10^{-3}$ dyne/2° twist. The length of the arcs l was measured directly and found to be 16·2 cm. The length of the loop, $2a$, was measured directly on the water. A polythene scale with two incisions a distance of $2a$ apart and a perpendicular arm was placed on the surface of the water. The two needles supporting the ends of the loop were placed in the incisions, the rod R was moved until the torsion arm was parallel to the perpendicular arm of the scale, and the zero position of the spot of light noted. A correction was made for the two polythene circles; $2a$ was equal to 14·6 cm.

The difference of surface pressure for a 2° twist of the torsion wire was $\pi = 3{\cdot}36 \times 10^{-3}$ dynes/cm./2°.

Cleaning the Surface.—It was found that even freshly distilled water contains an appreciable amount of surface-active material. This can be proved by spreading used mineral oil on the surface : a clean surface is completely covered by the oil which exhibits interference colours. The oil does not, however, spread completely on a contaminated surface, and the contaminated areas appear as black spots.

The surface could not be cleaned sufficiently with moving barriers for a variety of reasons. Guastalla (*loc. cit.*) describes a method where talc, previously cleaned by heating, is spread on the surface and then blown into a corner of the trough by a cleaned air stream, where it is sucked off together with the impurities and a little water. It was found, however, that the talc particles contaminated the film inside the loop and formed bridges across the fibre, causing slight leakage. The method adopted was to collect impurities in a corner of the trough by blowing with a clean air stream and to suck them off as in Guastalla's method. The process was repeated until the surface pressure attained a constant value.

The contamination of the surface was reduced to a minimum by carefully cleaning the air in the box, described above, the trough, and the liquid. A silica trough was used which, after being cleaned in the usual way, was heated to red heat before each experiment. The water used was distilled twice in an all-glass apparatus made of Pyrex glass, the second distillation being from a dilute solution of barium hydroxide as recommended by Guastalla. Under these conditions the rate of change of surface pressure was less than 1×10^{-3} dyne/cm./min.

Spreading of Films.—From the above it is clear that it is possible to study monolayers at these low pressures only when they are spread from a solution whose solvent either does not affect the surface tension or evaporates in 1—2 minutes. This condition is fulfilled with light petroleum (b. p. 70°) which, in amounts of 1 mm.^{3}/100 cm.^{2} evaporates in about 1 minute. The same amount of benzene appreciably altered the surface tension of water after 10 minutes, and the effect of acetone or amyl alcohol was detectable after an hour.

It is probable that some protein films may be completely spread from their solutions in water, but this has not yet been proved.

The *FA–F* curves obtained for myristic acid on N/100-hydrochloric acid and for the dibasic ester ethyl hexadecanedicarboxylate are shown in Fig. 4.

The work described was carried out in the Davy–Faraday Laboratory of the Royal Institution, London, and my thanks are due to Prof. E. K. Rideal, F.R.S., for suggesting the method and his kind encouragement and to Dr. R. S. Rivlin for his assistance with the mathematics involved. I would also like to thank the British Council for a scholarship which enabled me to carry out this work.

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