  NOTES *Bull. Chem. Soc. Jpn.*, **56**, 2525—2526 (1983)

A New Apparatus for Surface Pressure Measurements

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(Received March 23, 1983)

Synopsis. A new type of horizontal film balance is described. The principal features of the balance are the use of lightly paraffined silk threads without the conventional floating barrier of the Langmuir surface balance and of a strain gauge as the surface pressure detector.

For the measurement of surface pressures of insoluble monolayers at the air/water interface the Wilhelmy plate and the Langmuir float methods are generally used.[1] The Wilhelmy method has the advantage that no threads are required to close off the gaps at the end of the float used in the Langmuir method, but it has the drawback that contact angle changes can occur, particularly at high surface pressures. Our experience with the Wilhelmy method will be reported elsewhere, but we note here that it is particularly sensitive to inadequate control of temperature and relative humidity. Under appropriate conditions it may be used for micromanometry or higher pressure measurements, but cross-checking with the Langmuir method is generally required to rule out contact angle changes at the plate. Although the Langmuir float method does not suffer from the contact angle problem it requires considerable care. In particular, each of the threads between the float and the sides of the trough must be set up as an arc of a circle with the points of attachment to the float and side of the trough in a line at right angles to the side.[2] If the threads are mounted in other geometries spurious results are obtained.

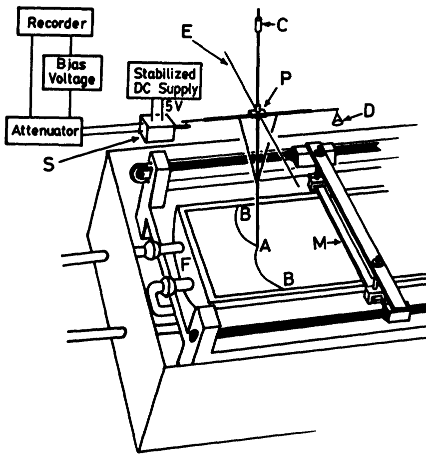

Fig. 1. Diagram of the horizontal surface balance. A is the end of the vertical arm of the frame; B, the edges of the trough; C, a counter weight; D, the calibrating pan; E, a torsion wire; P, a pivot; S, the strain gauge. The trough (F), is fitted with a glass tube for thermostatted water circulation and a driving system for the movable barrier (M) and is placed in a thermostatted box made of glass and aluminium plates. The ceiling of box is a glass plate which has a small hole for the vertical arm of the balance. The box and the balance are together installed in another thermostatted box.

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The present paper describes a new apparatus adopting a strain gauge as a detector for the surface pressure and which replaces the conventional float and thread system to separate monolayer and clean surface with a simple arrangement of threads.

Figure 1 shows a schematic drawing of the surface balance. A frame made of thin stainless steel tubes (diameters 0.75 to 1.66 mm) is attached to a tungsten torsion wire (diameter 0.33 mm) with a pivot block made of aluminium. The tubes and the pivot are fixed together by spot welding. The total weight of the frame and the pivot is 4.6 g. The strain gauge (type UL-2-240, Shinko Communication Industry Co. Ltd., Zushi, Japan) is connected to the end of the horizontal arm of the frame *via* thin tungsten wire. The effect of temperature on the strain gauge output is within $\pm 0.1\%/^\circ C$, and the total temperature effect on the calibration is *ca.* $0.2\%/^\circ C$. The sensitivity of the strain gauge is such that surface pressures were measured down to $0.05\ mN\ m^{-1}$. This is an excellent value, though can not be compared with a sensitivity limit of $50\ nN\ m^{-1}$ obtainable with the photoelectric detector described recently.[2]

The monolayer is confined between a movable hydrophobic barrier (M) and silk threads across the trough in place of the conventional float arrangement. The threads are $160\ \mu m$ in diameter. A pair is knotted together, cut off in equal lengths and immersed briefly in a solution of purified paraffin[3] in distilled hexane. The threads are mounted to form to equal arcs with the vertical arm (A) in the knot and the two ends attached to the sides of the trough with paraffin wax such that the ends and knot are in a straight line at right angles to the sides of the dish. Depending on the studies intended, the dish may be of silica or Pyrex glass hydrophobed with dimethyldichlorosilane.[4] With a little experience, the hydrophobing of the thread can be judged to give excellent resistance to monolayer leakage while remaining soft and flexible to allow the threads to adopt a circular profile when a surface pressure is applied.

The use of threads without a float to confine a monolayer has been reported previously, notably by Guastalla[5] and Kim and Cannell.[6] These workers used unequal arcs of thread so arranged that the restraining arm experienced a force in a direction across the trough which was read on a torsion wire mounted in a direction along the trough. This force can be amplified by making one (short) thread in the form of a semi-circle and the other (long) in the form of a shallow arc. The geometry of the arrangement must be measured exactly to

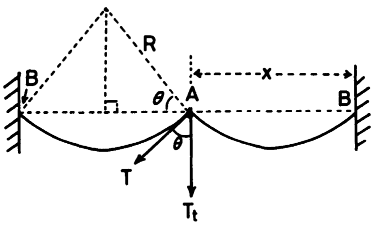

Fig. 2. Schematic drawing of the arc-shaped threads. A is the end of the arm of the frame; B, the edges of the trough; R, the radius of curvature of the threads; x, the distance A to B; T, the tension on the thread; T_t, the force on A along the direction of the trough and transverse to the torsion wire; θ, the angle between the direction of T and T_t.

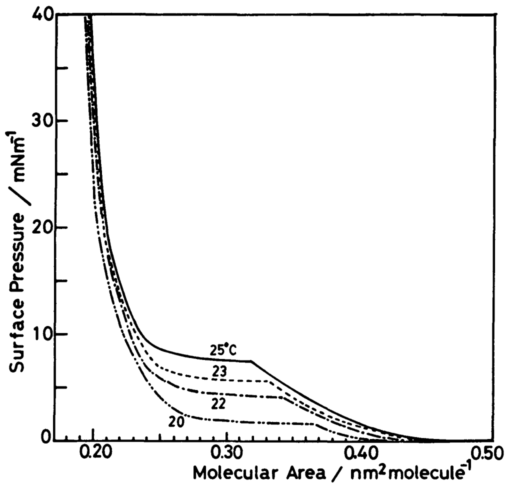

Fig. 3. Π-A diagrams for pentadecanoic acid on 0.01 mol dm^{-3} HCl at various temperatures.

convert the measured force to the surface pressure. With sensitive detectors, the use of these awkward geometried to obtain force amplification is unnecessary. The force may be read in the direction of the length of the trough and the geometry of the two equal threads used in our apparatus need not be known provided they adopt circular arc shapes with the length of each (l) conveniently in the middle of the range $\pi x > 2l > 2x$, where x is the half width of the trough and π is 3.14.

The force balance is shown in Fig. 2. For a given surface pressure Π, the tension in a flexible thread of radius of curvature R is given by the one-dimensional Laplace relation $T = \Pi R$. If each thread makes an angle θ to the direction along the trough, the force contribution in that direction (T_t) as read on the torsion balance is given by

$$T_t = 2T\cos\theta \tag{1}$$

and since

$$x = 2R\cos\theta \tag{2}$$

we have

$$\Pi = T_t/x. \tag{3}$$

The force read on the balance thus converts directly to surface pressure for all thread lengths in the required range. It will be obvious that if the threads are of unequal length, Eq. 3 may still be used provided that the ends and the arm (A) are again in a line at right angles to the sides of the trough. For lower pressures we have found that a single thread without a knot is convenient. The application of a surface pressure pushes the thread onto the arm, and it is sufficient to arrange the two sides approximately equal.

The surface balance was calibrated by suspending known weights from the horizontal arm of the system and measuring the voltage output of the strain gauge. The voltage output was found to be linear with applied force. Our experimental value for the surface pressure of an oleic acid (purity>99%) drop on the surface of 0.01 mol dm^{-3} HCl was good compared with that of Langmuir and Schaeffer.[7] Figure 3 shows typical Π-A diagrams for pentadecanoic acid on 0.01 mol dm^{-3} HCl; The diagrams are in agreement with reported[1] and our unpublished results which were obtained by using a conventional film balance with a float. The response of the new apparatus for a surface pressure change was superior to that of the float type film balance.

The observation of the time dependence of the surface pressure for pentadecancoic acid crystals sprinkled on the surface of 0.01 mol dm^{-3} HCl showed that the thread was resistant to film leakage at surface pressures up to 25 mN m^{-1} over a period of several days.

The authors wish to express their thanks to Miss Nobuko Maehara and Mr. Yoshihide Kaneko for their experimental assistances. The work was partially supported by a Grant-in-Aid from the National Science Foundation.

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