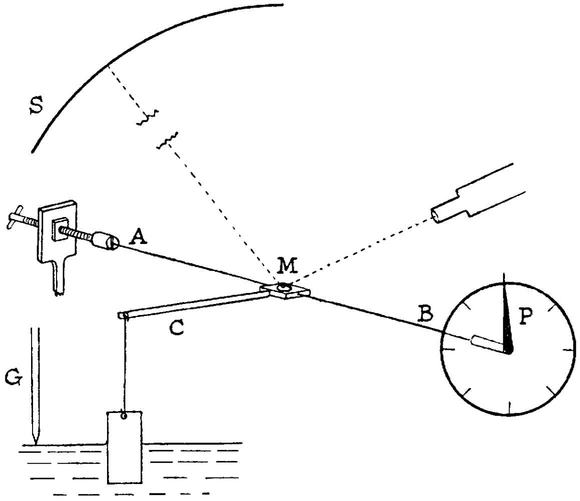
178. *The Properties of Freshly-formed Surfaces. Part VII. The Application of the Vertical-plate Technique to the Study of Soluble Films at Air–Liquid and Liquid–Liquid Interfaces.*

By C. C. Addison and S. K. Hutchinson.

The vertical-plate method, applied by previous workers to the study of insoluble monolayers, has been adapted for soluble-film measurements. In addition to single determinations of surface or interfacial tension, the method is suitable for time studies of short duration. The simple apparatus described is readily assembled, the essential features being a thin platinum plate and torsion wire. The procedure for ensuring zero contact angle is given. An accurate relation between the movement of the plate and the change in tension is calculated, and the theoretical calibration curves compared with those obtained experimentally. Advantages, and possible errors, arising from the wetting of the plate above the meniscus are discussed. Vertical-plate measurements involve the minimum of surface expansion during a determination, and the method has been developed with the object of comparing the results with those obtained at expanding surfaces (following papers).

The vertical-plate technique devised by Wilhelmy (*Ann. Physik*, 1863, **119**, 177) was developed by Harkins and Anderson (*J. Amer. Chem. Soc.*, 1937, **59**, 2189) and found to be at least as suitable for studying the compression of insoluble films as the horizontal-film balance, although Alexander and Teorell (*Trans. Faraday Soc.*, 1939, **35**, 1200) found the method limited in application. Dervichian (*J. Phys. Radium*, 1935, **6**, 221; *J. Chem. Physics*, 1939, **7**, 932) incorporated a device for the automatic recording of force–area curves. These workers maintained a constant vertical force on the plate by attaching it to one arm of an analytical balance. In Ruyssen's experiments (*Rec. Trav. chim.*, 1946, **65**, 581) on saponin solutions the vertical force was varied by means of a chainomatic balance, in order to maintain the plate in the same position with respect to the surface, thus eliminating the buoyancy factor. Andersson, Ställberg-Stenhagen, and Stenhagen (" The Svedberg ", Almqvist and Wiksells, Uppsala, 1944) replaced the analytical balance by a torsion wire, and employed automatic recording. To overcome variations in contact angle at liquid–liquid interfaces, Alexander and Teorell (*loc. cit.*) suggested that the plate be made uniformly hydrophobic by depositing a film of ferric stearate, and Cheesman (*Arkiv Kemi, Min. Geol.*, 1946, **22***B*, i, 1) has successfully employed a uniform coating of carbon for this purpose.

FIG. 1.



These modifications of the vertical-plate technique have been developed primarily for the study of insoluble monolayers. The method has been little used in work on soluble films, probably because for pure liquids and many solutions it offers few, if any, advantages over the many other simple and accurate methods already available for surface-tension measurement. However, in the course of experiments on the expansion of soluble films (Parts VIII and IX, following papers) it became necessary to determine the surface tension of various solutions under conditions involving minimum expansion of the surface. Several of the standard methods for surface-tension measurement involve considerable expansion of the surface either during the determination (*e.g.*, drop-weight and bubble-pressure methods) or at the moment when the tension is recorded (*e.g.*, the ring method). The vertical plate does not suffer from this disadvantage, and the surface tensions can be derived without the use of empirical correction factors.

In adapting the technique to soluble-film measurements, the following considerations are important. (1) The relative positions of the plate and the surface must be easily adjustable, to ensure zero contact angle; (2) when the method is used for the study of rates of adsorption, decreasing tensions are involved (these conditions resemble the compression of insoluble monolayers, but high sensitivity is essential); (3) during expansion of a soluble film, the tension rises (therefore the instrument should be capable of recording tension during the falling of the plate). The torsion-wire technique described below satisfies these requirements, and the apparatus may be readily assembled from material normally available.

EXPERIMENTAL.

The arrangement of the apparatus is shown diagrammatically in Fig. 1. The torsion wire *AB* was of phosphor-bronze, 0·032 cm. in diameter, 23 cm. long, and was free from fatigue. The end *A* was held in a chuck attached to a screw, and was fixed in position by means of locking nuts. The lever arm *C* was of aluminium, 11 cm. long. The plate was supported by a platinum wire which passed loosely through holes in arm C and the plate, thus ensuring that the plate remained vertical during a determination. Measurements were conducted with both glass and platinum plates, and were found to be more reproducible when platinum was used; this was attributed to the greater ease with which the platinum surface could be cleaned; between each measurement the plate (2·24 cm. wide, 5 cm. long, and 0·0033 cm. thick) was washed with distilled water, wiped with a fine cloth, washed again, and heated in a flame to a white heat.

Movement of Plate.—The variation in the position of the plate produced by change in surface tension was magnified by attaching a mirror M to the junction of the arm C and the torsion wire. A spotlight and hair-line were reflected on to a circular scale S, arranged with its centre at M and 84·5 cm. distant, giving a magnification of about 15.

Position of Surface.—In preliminary experiments the surface was maintained at a constant and predetermined level by viewing it through a microscope carrying an eye-piece scale. In view of the difficulty of setting a liquid–liquid interface accurately by this method, it was found more convenient (and sufficiently accurate) in later experiments to raise the level of the liquid to the tip of a glass rod G drawn to a point. Two such rods were used in work at liquid–liquid interfaces. For the study of time or surface-expansion effects the liquid may be contained in a trough. For single measurements on a series of solutions, a circular (inverted conical) vessel, giving a liquid surface 15 cm. in diameter, was used. This vessel carried a run-off tap, so that the liquid could be completely drained away and the vessel refilled with fresh solution to the tip of the glass rod. The vessel carried a transparent cover (slotted to accommodate the glass rods and plate suspension wire) to minimise evaporation.

Position of Plate.—The position of the plate with respect to the surface was controlled by the pointer P, to which the end B of the torsion wire was attached. P moved freely over a 360° dial, and carried a lens for accurate setting.

Discussion and Results.

A vertical platinum plate, width w and thickness t, when partly immersed to a depth l in water of density d and surface tension γ, will attain a position of equilibrium when the weight W_g of the plate, plus the surface tension acting on it, are balanced by the upthrust of the water, plus the vertical force F due to the torsion wire. Thus

$$2(t + w)\gamma + Wg = twdlg + F \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

In any series of measurements the setting of pointer P is standard, so that both ends of the torsion wire are fixed in position. The force F exerted by the torsion wire depends upon, and varies with, the vertical movement of the plate and the lever arm C. It is convenient to arrange the initial setting of end A of the wire so that the wire has a clockwise torque in the direction $A \longrightarrow B$ (Fig. 1), in which case lifting of the plate involves decrease in the torsion. The fact that the torque in the two halves of the wire AM and MB is not altered to the same extent by change in position of C is immaterial.

If the water is replaced by a solution of a surface-active agent (sufficiently dilute that the density is not appreciably affected) the plate will rise out of the liquid a distance Δh until the decrease $\Delta\gamma$ in tension is balanced by the decrease in buoyancy, plus the decrease in F. Thus

$$2(t + w)\Delta\gamma = twdg\Delta\mathrm{h} + \Delta F \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Δh is magnified on the scale S. If ΔS represents the difference between the scale readings for pure water and for the solution, then $\Delta S = 2y\Delta h/x$, where x is the length of arm C and y is the distance MS. Therefore

$$\Delta\gamma = K_1\Delta S + K_2\Delta F \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where $$K_1 = twdxg/4y(t + w) \text{ and } K_2 = 1/2(t + w)$$

K_1 and K_2 are therefore constants of the apparatus, and had values 0·105 and 0·223 respectively for the apparatus and settings employed.

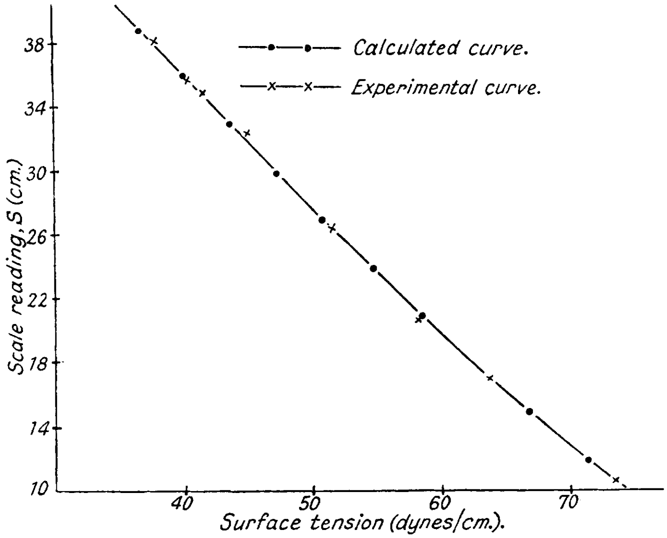
In order to relate $\Delta\gamma$ and ΔS, it is necessary to obtain ΔF in terms of ΔS. The assumption that ΔF and Δh (and thus ΔS) are proportional is only justified for very small values of Δh. To avoid this assumption, the pointer P was fixed at the standard position, known weights suspended from the end of arm C, and the S–F relation graphed directly. From this accurate curve, the F values corresponding to the S readings for water and solution can be obtained. The difference between these F values is the ΔF term of equation (3). It will be clear from the above calculations that water is not a necessary standard. Any solution may serve as standard, provided that its surface tension under the static conditions of the experiment be known.

Sensitivity.—The sensitivity of the apparatus (*i.e.*, $\Delta S/\Delta\gamma$) may be controlled by three methods : (*a*) by adjustment of the length of arm C and the mirror-scale distance, (*b*) by varying the dimensions of the plate, and (*c*) by using different torsion wires, thus varying the significance of the ΔF term in equation (3).

Method (*a*) is undesirable since it involves structural alterations to the apparatus; method (*b*) provides the widest range of sensitivity. In studying changes of surface tension with time, tension ranges up to 30 dynes/cm. may be encountered, and it is essential to adjust the sensitivity of the apparatus to the anticipated tension range. Maximum sensitivity was therefore obtained by employing the thinnest platinum plate consistent with rigidity (0·0033 cm. thickness was found suitable), and this high sensitivity was then diminished where necessary by changing the torsion wire. It is a major advantage of the present technique that the same plate may be used throughout an investigation, irrespective of sensitivity.

Applicability of Equation (3).—The γ–S relation has been calculated by using equation (3), and compared with that obtained by direct measurement of γ and S for a series of *iso*amyl alcohol solutions at 15°. In deriving the theoretical curve, water was taken as standard, γ being taken as 73·6 dynes/cm. at 15°. *iso*Amyl alcohol was selected as solute because the surface tension of its solutions reaches the static value within 0·1 sec. (Addison, *J.*, 1944, 252). Again, drop-weight measurements at various flow rates have shown that the solutions are not influenced by surface expansion, and therefore the surface-tension values obtained by the drop-weight method are also those operating at the static surfaces used in the vertical-plate experiments. Fig. 2 indicates that agreement is good, and that equation (3) correctly interprets the behaviour of the vertical plate at the air–water interface.

FIG. 2.

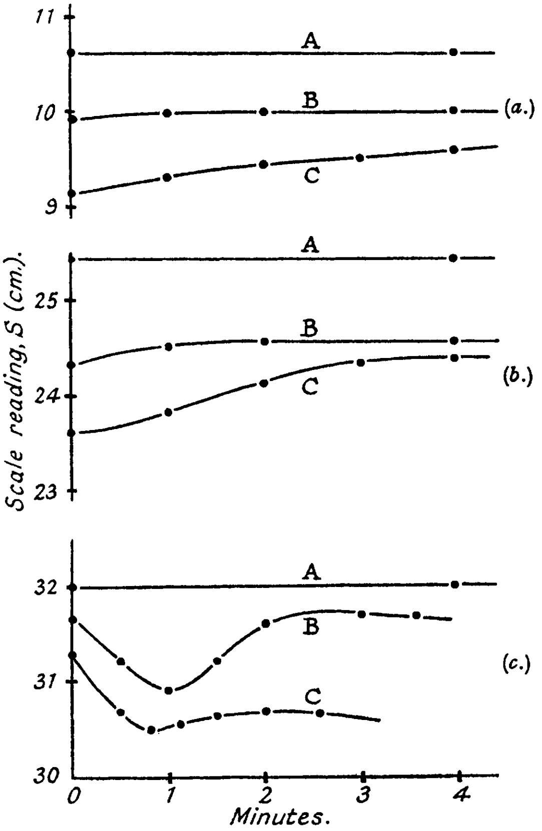


Wetting of the Plate.—To obtain reproducible values for $\Delta\gamma$, the plate was partly immersed in the liquid, and then raised until zero contact angle was obtained; the zero angle was readily observed by direct viewing of the plate. Again, when pointer P was moved at a uniform rate, the movement of the spotlight over scale S was erratic until the contact angle became zero; thereafter, its movement was smooth. If the plate is raised beyond the distance necessary for the formation of zero contact angle, it supports a film of liquid above the meniscus. With thin plates, the weight of this film introduces an error into the readings, the drainage of the film gives rise to a drift in the S value with time, and close control over the distance through which the plate is raised after initial immersion is therefore essential. In each determination, pointer P was set at an angle below the standard position at which the apparatus was calibrated, and the plate gently lowered into the liquid. The pointer was then raised to the standard position, and the length of wetted plate was thus determined by the extent of this final adjustment of P. Figs. 3(*a*), (*b*), and (*c*) show the drifts obtained with water and *iso*amvl alcohol solutions: the approximate length of wetted plate, and the angle representing final adjustment of P, are given for each curve. With distilled water, a length of wetted plate exceeding about 0·5 cm. gave rise to drainage drifts, and the weight of liquid in 0·5 cm. of film introduces an error of about 0·6 dyne/cm. into the tension reading. Similar results were obtained with 0·5% *iso*amyl alcohol solutions, but at higher concentrations of alcohol (Fig. 3, *c*) any exposure of wetted plate gave rise to erratic readings. Ridges of solution were observed to rise and fall on the wetted portion of the plate above the meniscus, and may be of the type studied by Satterly and Stuckey (*Trans.*

Roy. Soc. Canada, **1932**, **26**, 131). In no case was a drift obtained when the plate was raised just sufficiently to ensure zero contact angle.

Measurement of Increasing Tensions.—A technique similar to the above may be employed in the study of increases of surface tension over short time intervals. The plate is wetted to a distance slightly in excess of that which it is anticipated the plate will fall during the experiment. Provided that the time intervals are so short that the liquid film on the plate does not evaporate, a zero contact angle is maintained during the falling of the plate. If the error in the tension readings (less than 1 dyne/cm.) due to the presence of the liquid film on the plate is significant in comparison with the tension range involved, it may be calculated from the known length of wetted plate, and the values corrected.

FIG. 3.



(a) *Water.*
(b) 0·5% iso*Amyl alcohol solution.*
(c) 1% iso*Amyl alcohol solution.*

Curve.	Length of wetted plate, cm.	Pointer adjustment.
A	0—0·1	5°
B	0·5	10
C	1·0	15

Liquid–Liquid Interfaces.—The procedure outlined above has been successfully applied to liquid–liquid interfaces. The plate was suspended partly in the lower aqueous phase, and partly in the upper oil layer, and only the suspending wire penetrated the oil surface. As the interfacial tension decreases, the plate again rises until $\Delta\gamma$ is balanced by (*a*) the decrease in buoyancy forces on the plate at the interface, and on the wire at the oil surface, and (*b*) the decrease in F. Thus for zero contact angle

$$2(t + w)\Delta\gamma = tw\Delta h(d - d_2)g + \pi r^2 d_2 g\Delta h + \Delta F$$

where d_2 = density of the oil and r = radius of the suspension wire. This reduces to

$$\Delta\gamma = K_3\Delta S + K_2\Delta F \qquad . \; . \; . \; . \; . \; . \; . \; . \qquad (4)$$

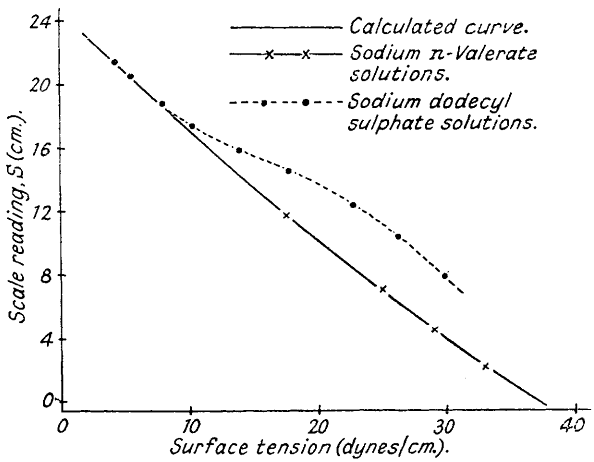
K_2 has the same value as in equation (3), and K_3, which is again a constant of the apparatus, has the value

$$[tw(d - d_2)gx + \pi r^2 x d_2 g]/4y(t \times w)$$

thus including both buoyancy factors.

To obtain zero contact angle, close control over the position of the plate with respect to the interface is again essential, and it was found necessary at interfaces to raise the plate through approximately twice the distance required at the air–liquid interface, before the contact angle fell to zero. With all aqueous solutions tested, the meniscus crept down the plate when the latter was raised beyond the distance required for formation of a zero contact angle, so that at interfaces no " wetted-plate " difficulties arise. With solutions of strongly surface-active substances, no detectable alteration in contact angle occurred during 15 minutes, so the apparatus may be applied to time studies of short duration. With water and solutions of high interfacial tension, the contact angle increased irregularly over several minutes, but remained at zero for a sufficient time (30—60 seconds) after the initial lifting of the plate to enable an accurate reading of the interfacial tension to be taken. To conduct time studies of short duration with the latter solutions, the sensitivity of the apparatus may be increased so that the distance through which the plate rises as tension decreases is sufficient to maintain a zero contact angle. However, it has not been found possible to maintain zero contact angle at the interface as the plate falls, so that with the present apparatus time studies involving increase in tension are restricted to the air–liquid interface.

FIG. 4.



By employing equation (4), the theoretical γ–S curve has been calculated (Fig. 4), the water–toluene interface being used as standard, and γ being taken as 36·6 dynes/cm. at 15°. Under these conditions K_3 = 0·0375. To confirm the applicability of this calibration curve, S values were measured for a series of sodium dodecyl sulphate solutions. The drop-volume method was used in determining the interfacial tensions because of its accuracy. The broken curve (Fig. 4) shows that agreement is ideal at tensions below 8 dynes/cm., but that at higher values a considerable discrepancy arises. A subsequent investigation (Part IX) has shown that for these more dilute sodium dodecyl sulphate solutions the interfacial tension at an expanding surface (*i.e.*, as recorded by the drop-volume method) is appreciably higher than that at a stationary surface. This expanding-surface effect is only operative at concentrations below 0·005M, and it is of interest that this is also the concentration below which the discrepancies (Fig. 4) occur.

To confirm the theoretical curve over the higher tension ranges it was therefore necessary to employ a short-chain solute. As with air–liquid interfaces, the liquid–liquid interfacial tension of such solutions is not influenced by surface expansion, and the tension values measured with accuracy by the drop-volume method are again those operating on the vertical plate. However, most short-chain alcohols and carboxylic acids have appreciable solubility in toluene, and the hydrolysis of salts of aliphatic carboxylic acids also gives rise to migration of acid across the interface. These difficulties were overcome by dissolving *n*-valeric acid in 2N-sodium hydroxide solution, and diluting the solution with 0·1N-sodium hydroxide solution to suppress hydrolysis. The densities of the solutions were then restored to that of water by further slight dilution or addition of alkali. By this means stable S readings were obtained over the tension range 17—36·6 dynes/cm. (employing up to 6% *n*-valeric acid) and the γ–S points in this range are recorded in Fig. 4. Agreement with the theoretical curve is ideal, and equation (4) therefore interprets correctly the behaviour of the vertical plate at liquid–liquid interfaces.

UNIVERSITY COLLEGE, NOTTINGHAM.

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