about 0.02 or 0.03 Å. The increase observed is from 0.04 to 0.08 Å. Accordingly, an explanation in addition to the mutual repulsion of the atoms is necessary. The distortion of the benzene ring discussed above occurs in these unsymmetrical compounds in a manner which would increase the ortho chlorine atom separations from 0.02 to 0.04 Å. according to the deviations from 120° of the various ring angles. Although still other effects may be involved it seems probable that some of the increase is to be ascribed to distortions of the benzene ring.

It should be noted that even if a regular benzene ring is assumed the bending of the carbon–chlorine bonds is not large. In *o*-dichlorobenzene the bending calculated with a regular ring is less than 1°; in 1,2,4,5-tetrachlorobenzene it is 1.5°. The distortion of the bond angles is much less than has been estimated on the basis of dipole measurements, in the interpretation of which insufficient allowance was made for the interaction of the moments in the adjacent carbon–halogen bonds.

We are grateful to Professor Linus Pauling for his encouragement and advice during the course of this investigation.

Summary

The molecular structures of some of the chlorobenzenes have been investigated with the following results

Substance	Sum of C–C and C–Cl, Å.	C–C (assumed), Å.	C–Cl, Å.	Cl–Cl (ortho), Å.	Cl–Cl (meta), Å.	Cl–Cl (para), Å.
C_6Cl_6	3.11	1.41	1.70	3.11	5.39	6.22
1,3,5-$C_6H_3Cl_3$	3.10	1.41	1.69		5.38	
m-$C_6H_4Cl_2$	3.09	1.40	1.69		5.35	
p-$C_6H_4Cl_2$	3.09	1.40	1.69			6.18
C_6H_5Cl	3.08	1.39	1.69			
o-$C_6H_4Cl_2$	3.11	1.40	1.71	3.15		
1,2,4,5-$C_6H_2Cl_4$	3.12	1.40	1.72	3.20	5.37	6.25

The decrease of the carbon–chlorine distances below the value 1.76 Å. observed in the chloromethanes is due to the contribution of electronic structures which introduce a degree of double bond character in the carbon–chlorine bonds. The resonating structures involved produce distortions in the benzene ring amounting in some cases to an increase of 0.02 Å. in the carbon–carbon distances. The benzene ring distortion is responsible in part for the increased chlorine–chlorine separation observed in the unsymmetrical ortho substituted compounds. The distortion of the bond angles in the ortho positions is not as great as has been supposed previously; even with the assumption of a regular benzene ring the ortho bonds are bent to the order of 1°.

Pasadena, Calif. Received August 17, 1937

[Contribution from the George Herbert Jones Chemical Laboratory of the University of Chicago]

I. A Simple Accurate Film Balance of the Vertical Type for Biological and Chemical Work, and a Theoretical and Experimental Comparison with the Horizontal Type. II. Tight Packing of a Monolayer by Ions

By William D. Harkins and Thomas F. Anderson

Introduction

The importance of the determination of pressure–area relations of monomolecular films in biological problems and other work in surface chemistry makes the development of new methods for such investigations desirable. This is particularly true in view of the disadvantages of the "horizontal pull" film balance[1] now in use. This apparatus is too inaccurate in its crude form and too difficult to build and to operate in its precision form to be adopted widely by either biologists or chemists. Furthermore, it is difficult to avoid the use of metals in its construction and their presence makes the device unsuitable for a study of the effects of metallic ions on surface films.[2] It is also difficult to adapt the instrument for continuous compression of surface films. Continuous compression is highly desirable to simplify the mathematical theory of the observed effect of the rate of compression on the pressure–

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(1) So called because it measures a horizontal force. In the adaptation of the Wilhelmy surface tension balance for the study of surface films which is to be described here, a vertical force is measured. This latter device is therefore designated the "vertical pull" film balance.

(2) W. D. Harkins and H. Zollman, This Journal, **48**, 69 (1926); I. Langmuir and V. J. Schaefer, *Science*, **34**, 379 (1936); Abstracts of Papers Presented before Div. of Phys. and Inorg. Chem. of Am. Chem. Soc. at 93rd Meeting, Chapel Hill, N. C., April 12, 1937; R. J. Myers and W. D. Harkins, *Nature*, **139**, 367 (1937); J. S. Mitchell, E. K. Rideal and J. H. Schulman, *ibid.*, **139**, 625 (1937).

area curves of films of the higher fatty acids[3] and of certain films, such as those of the five-ring compounds, which exhibit an extremely marked rearrangement on compression.[4]

The "horizontal pull" film balance has the advantage of being a differential method of measuring surface pressures. That is, it measures directly the difference $-\Delta\gamma$ between the surface tension of a clean water surface γ_W and that of a surface covered by a film γ_F.

The problem is to find a differential method which does not possess the above disadvantages.

An attempt in this direction has been made by Lee and Wu, and by Gorter and Seeder[5] who, however, have been unable to check the "horizontal pull" film balance by the ring method.[6]

A modification of the Wilhelmy method for the determination of surface tensions[7] seemed to give promise of being a differential method of great simplicity for the study of surface films. Such a method has been used by Dervichian[8] for the study of the behavior of surface films under rapid continuous compression. However, he has done no work which indicates whether the method gives reliable results.

In this paper it is shown from the agreement between results of simultaneous determinations of surface pressures by this "vertical pull" film balance and the "horizontal pull" film balance, that, when properly used, this method gives as accurate, and, for some purposes, more accurate, results than even the precision form of "horizontal pull" film balance. Besides its simplicity the method possesses a number of advantages. (1) The use of metals or glass in contact with the film is easily avoided. Quartz alone may be used in the study of the effects of metallic ions on surface films. (2) It may be adapted easily to a continuous compression of the film. (3) The operation and recording of the instrument may be made automatic as has been done by Dervichian.

The simple theory of the "vertical pull" as well as that of the "horizontal pull" balance is given. This latter theory, which has not been developed before, is complicated by the fact that the water surface is curved near the float of the balance.

The authors wish to thank Professor E. Emmet Reid for a generous supply of the exceedingly pure stearic acid[9] used in this investigation.

Description and Theory of Apparatus

The Wilhelmy Surface Tension Balance.—The Wilhelmy method of determining surface tensions[7] consists in measuring directly by means of a balance the pull of the surface of the liquid on the perimeter of a body such as a vertical microscope slide partially immersed in the liquid. If w is the width of the slide and t is its thickness, its perimeter is $2(t + w)$. Then if the angle of contact is ϑ and γ is the surface tension, the vertical force due to the pull of the surface tension on the slide is $2\ \gamma(t + w) \cos \vartheta$. Now the force due to buoyancy, equal to the weight of the water displaced, is $-g\rho ltw$ where g is the acceleration of gravity, ρ is the density of the liquid, and l is the depth of immersion of the slide. If now W is the weight of the free dry slide and G is the apparent weight of the partly immersed slide, the following equation holds at equilibrium

$$gG = gW + 2\gamma(t + w)\cos \vartheta - g\rho ltw \qquad (1)$$

In many cases $\vartheta = 0$ and Eq. (1) can be written in the form

$$\gamma = \frac{g(G - W + \rho ltw)}{2(t + w)} \qquad (2)$$

As a rough check of the accuracy of the method it was used to determine the surface tension of water and that of benzene at 25.00°. The term which contains l, the depth of immersion, was eliminated in the method used by determining the exact point (± 0.001 cm.) at which the horizontal lower edge of the slide touched the water surface ($l = 0$) and then determining the weight G necessary to bring the edge back to this point from the interior of the liquid. The surface tensions observed were 71.78 ± 0.08 and 28.81 ± 0.07 dynes/cm. for water and benzene, respectively, while the accepted surface tensions are 71.97 ± 0.05 and 28.22 ± 0.05 dynes/cm., respectively. Undoubtedly the accuracy of these measurements could have been improved.

The Vertical Pull Film Balance.—The Wilhelmy method just described may be modified easily for use as a film balance. A rectangular shallow trough of quartz, Pyrex glass, or metal is

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(3) W. D. Harkins and R. J. Myers, *J. Chem. Phys.*, **4**, 716 (1936).

(4) W. D. Harkins, E. F. Carman and H. E. Ries, THIS JOURNAL, **58**, 1377 (1936); F. A. Askew, *J. Chem. Soc.*, 1587 (1936).

(5) W. Y. Lee and H. Wu, *Chinese J. Physiol.*, **16**, 307 (1932); E. Gorter and W. A. Seeder, *Kolloid-Z.*, **61**, 246 (1932).

(6) This method is unsuitable for surface films since the area per molecule of the film inside the ring changes more rapidly than that outside as the ring is lifted from the surface. Therefore the surface pressure outside the ring is different from that inside at the time the measurement is made and an incorrect surface pressure is observed.

(7) L. Wilhelmy, *Ann. Physik*, **119**, 177 (1863); A. Frumkin, *Z. physik. Chem.*, **116**, 466 (1925).

(8) D. G. Dervichian, *J. Physique*, [7] **6**, 221 (1935).

(9) J. D. Meyer and E. E. Reid, THIS JOURNAL, **55**, 1574 (1933).

used to hold the water upon which the film is spread. The edges of this trough are paraffined, and the surface is swept by barriers of quartz or Pyrex glass. The film is confined by the two side edges of the trough and by a barrier, which consists of a strip of quartz or Pyrex glass, at each end. One of these barriers is moved to compress the film. This trough is contained in an air thermostat. An analytical or a pulp balance is mounted on the top of the thermostat, and a fine aluminum rod is suspended from the pan hook of the balance. This rod passes through a hole in the bottom of the balance and another in the top of the thermostat. The microscope slide is suspended vertically at the bottom of the rod.

The deflection of the balance beam may be read on a scale by the position of a beam of light reflected from a galvanometer mirror fastened to the beam of the balance. The slide is suspended, partially immersed in the water in the trough. The zero point reading of the scale is taken while the water surface is clean. A ligroin or benzene solution of the material of which the film is to be formed is now spread on the surface of the water. The volatile solvent evaporates, leaving behind the film on the water surface. This film is then compressed. This lowers the surface tension, so the slide rises and this deflects the beam of the balance. This deflection is proportional to the quantity $-\Delta\gamma \equiv \gamma_W - \gamma_F$ or the surface pressure, as is shown from the simple theory presented below.

From Eq. (1) we may write when $\vartheta = 0$

$$g\Delta G = 2(t + w)\Delta\gamma - g\rho tw\Delta l \qquad (3)$$

Thus if the weight G is held constant ($\Delta G = 0$), the change in surface tension $\Delta\gamma$ will be proportional to the change in the depth of immersion of the slide Δl, which can be measured directly by means of a cathetometer. In the present case it was found to be convenient to mount a galvanometer mirror on the beam of the balance and observe deflections of the beam by means of a telescope and illuminated millimeter scale. For small deflections of the beam Δl is proportional to ΔS, the change in the scale reading. We then have

$$g\Delta G = 2(t + w)\Delta\gamma - k\Delta S \qquad (4)$$

where k is the factor of proportionality.

The calibration of the Wilhelmy balance consisted in determining the proportionality factor k by noting deflections of the balance beam ΔS for added weights ΔG on the balance pan with the slide partially immersed in a clean water surface ($\Delta\gamma = 0$). Then we have the relation

$$k = -g\Delta G/\Delta S \qquad (5)$$

The factor k was constant within experimental error (±0.5%) in the 2.5° range of deflections employed.

The reductions of the surface tension $\Delta\gamma$ caused by spreading and compressing a surface film can then be determined by noting the beam deflections ΔS while the weight on the pan is kept constant ($\Delta G = 0$). The equation for $\Delta\gamma$ is then

$$\Delta\gamma = k\Delta S/2(t + w) \qquad (6)$$

The microscope slides used were approximately 2.5 × 0.1 cm. in cross section and were marked "chemically resistant." With these slides a change in surface tension of 1 dyne/cm. corresponded to a change of 5 mg. in the weight on the pan or 0.8 cm. in the scale reading. The scale could be read to ±0.01 cm. Much greater sensitivity could have been obtained by the use of thinner slides, but the advantage thus gained would have been partly nullified by the excessively large deflections which would have been obtained for large pressure. The slide was held in a vertical position by a nichrome clip. To damp the oscillations of the slide a piece of microscope slide was attached in a horizontal position to the lower end of the measuring slide.

This apparatus has the advantage of being simple and inexpensive. Made so that only quartz or Pyrex glass comes in contact with the film and substrate, it is particularly suitable for the study of the effect of traces of metal ions. It easily can be made automatically recording for the study of the behavior of films under continuous compression.

The Horizontal Type of Film Balance.—The torsion film balance was similar to that used by Harkins and Myers[3] except that the divided circle for the measurement of the angle of torsion of the wire was mounted directly on the turning clamp which held the wire. Since one purpose of the present work is to investigate the accuracy of the film balance a brief account of the theory of this balance is presented together with an estimate of the probable errors in the measurement of forces and areas.

Measurements with the film balance consist in the determination by some means such as a torsion balance of the total horizontal force per centimeter F_H which acts on a paraffined uniform strip or float (F in Fig. 1) which rests on a water surface. The horizontal force per centimeter due to the freshly swept water surface on one side of the float is $\gamma_w \cos A_w$ where γ_w is its surface tension and A_w is the angle of inclination of the surface to the horizontal at the point of contact. Similarly the force per centimeter in the opposite direction due to the water surface on the other side of the float on which a surface film has been spread is $-\gamma_F \cos A_F$. If Z_w is the depth of the line of contact of the pure water surface with the float below the horizontal water surface and Z_F is the depth of the line of contact of the film covered surface with the float, the horizontal force per centimeter due to the pressure of the water on the float is $^1/_2\, g\rho_w (Z_w + Z_F)(Z_w - Z_F)$. Here ρ_w is the density of the water. The total horizontal force on the float is then given by the equation

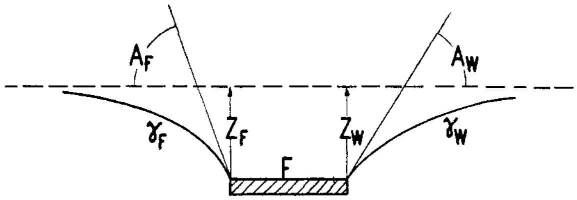

Fig. 1.—Cross section view of float of the film balance (horizontal type) on water surface. The freshly swept water surface is on the right and the film covered surface is on the left.

$$F_H = L[\gamma_w \cos A_w - \gamma_F \cos A_F + {}^1/_2 g\rho (Z_w + Z_F)(Z_w - Z_F)] \quad (7)$$

where L is the length of the float.

Now the equation of the cross section of the water surface taken perpendicular to the float is

$$z_w^2 = 2\gamma_w(1 - \cos\alpha_w)/g\rho \quad (8)$$

where α is the angle of inclination of the surface at the point z_w. A similar equation holds for the film covered surface

$$z_F^2 = 2\gamma_F(1 - \cos\alpha_F)/g\rho \quad (9)$$

At the line of contact between the float and the liquid surface $z_w = Z_w$, $\alpha_w = A_w$, $z_F = Z_F$, and $\alpha = A_F$ in Eqs. (8) and (9). There are then obtained the relations

$$\cos A_w = 1 - \frac{\rho g}{2\gamma_w} Z_w^2$$

$$\cos A_F = 1 - \frac{\rho g}{2\gamma_F} Z_F^2$$

Inserting these values for $\cos A_w$ and $\cos A_F$ in Eq. (7) we obtain the relation

$$F_H = L\left[\gamma_w\left(1 - \frac{\rho g}{2\gamma_w} Z_w^2\right) - \gamma_F\left(1 - \frac{\rho g}{2\gamma_F} Z_F^2\right) + {}^1/_2 g\rho (Z_w^2 - Z_F^2)\right]$$
$$= L[\gamma_w - \gamma_F] \quad (10)$$

The horizontal force on the float is thus simply its length times the difference in surface tensions and is independent of the tilt of the float or the way the liquid surface wets its surface.

There is one source of error in the actual magnitude of the force on the float, namely, it is assumed that the gold or platinum ribbon which prevents the film from passing around the float is perfectly uniform, and that the force acting on the ribbon is divided equally between the float and the stationary part of the film balance. Inasmuch as the ribbon must be paraffined to prevent its being wet by the water, this is a difficult situation to attain. In the present case the float was approximately 23 cm. long and the distance between posts was about 25 cm., so the assumed effective length was about 24 cm. The maximum error possible would be therefore ±1 cm. or about ±4% of the length of the float. The actual error due to this uncertainty is probably much less than ±1%.

More serious errors are introduced in the measurement of the force on the float. The worst of these is probably the uncertainty in the length of the lever arm of the force F_H which is the distance between the float and the torsion wire. This distance is affected by three factors: the height of the water surface, the fact that the float is not perfectly horizontal, and the change in the depth to which the float sinks as the surface tension of the film covered surface decreases on compression. It is impractical to measure all of these varying factors during a force–area determination. Assuming the uncertainty in the distance between the float and the torsion wire to be ±1 mm., the systematic error thus introduced in the force measurements is ±2%. Other factors which affect the accuracy are the error in setting the instrument on the zero point and the error in reading the angle of torsion of the wire. The total random error in pressure measurements thus introduced is at least ±0.06 dyne/cm. while the total systematic error may be as great as ±3% of the pressure.

Measurement of the Area per Molecule.—Errors in the measurement of the area per molecule are quite distinct from errors in the measurement of $-\Delta\gamma$. The dimensions of the trough and the position of the movable barrier can be measured so accurately that the error in the measurement of the total area of the trough is less than ±0.1%. Also, the solution of the material to be spread easily can be made up to a concentration which is known to 0.1%. The principal error is in the determination of the amount of material spread. Dr. G. C. Nutting of this Laboratory used a weight pipet similar to that described by Harkins and Myers[3] in a series of four careful determinations of the area of stearic acid on 0.01 N hydrochloric acid. He obtained low limiting areas per molecule (22.4 sq. Å.) which had a mean deviation from the mean of 2%. Errors of this magnitude are unsatisfactory in the precise study of metallic ions on surface films, so it was decided that a volumetric pipet would be substituted.

The use of an automatic micro-volume pipet was kindly suggested by Dr. Katherine B. Blodgett. Of the two designs constructed, that indicated in Fig. 2 was found to be the more accurate and the easier to operate. In its use the liquid to be measured is drawn into the capillary tube T by means of a medicine dropper bulb B until it overflows from the fine capillary tip at E_1. Then when the end of the fine capillary tip E_2 is removed from the solution the liquid remains in the capillary tube until the bulb is squeezed. The use of fine capillary tips has a three-fold purpose: first, the amount of liquid held between the two tips is reproducible; second, the liquid is held automatically between the tips by capillary action; and, third, any creeping of the liquid around the lower tip causes a relatively small loss of solute due to evaporation of the solvent from the small surface area.

With an 0.18-ml. pipet of this design the mean deviation from the mean volume delivered in a series of determinations was 0.05% while that for a 0.09-ml. pipet was 0.14%. When the 0.18-ml. pipet was used for measuring the amount of solution, Dr. Nutting found the extrapolated area at zero compression of a film of stearic acid at 25° on 0.01 N hydrochloric acid to be 23.80 sq. Å. per molecule and the mean deviation from the mean of eight determinations to be 0.08 sq. Å.

Experimental Procedure and Technique

In order to make simultaneous measurements of film pressures by the two methods, the balance for the Wilhelmy determination of surface pressures was placed on top of the thermostat box which contained the torsion film balance. Simultaneous measurements of surface pressures were made on films of lecithin, pentadecylic acid, stearic acid, and calcium stearate. Since the film balance was used for the comparison the substrate was placed in the ordinary chromium plated brass trough coated with paraffin. Paraffined brass barriers were used.

Probably the most exacting feature of the technique of the Wilhelmy method is the achievement of a zero contact angle ϑ. If $\vartheta = 0$ Eq. (2) or Eq. (4) can be used for the determination of $-\Delta\gamma$. Otherwise ϑ itself must be measured and Eq. (1) used.

To insure zero contact angle a number of precautions must be taken. First, the slide must be clean. In the present case the slide was washed in a hot solution of sodium dichromate in concentrated sulfuric acid, rinsed in distilled water and kept in 1 N sodium hydroxide when not in use. Before use it was washed with distilled water and then rinsed with a sample of the solution in which it was to be used. Excess drops of the solution were removed with filter paper before the slide was partially immersed in the solution in the film balance tray, the surface of which had been freshly swept. The zero point was then determined, and to avoid contamination the slide was lowered into the surface before the solution of the surface active material in ligroin or benzene was spread. The slide was then allowed to rise to the new equilibrium position corresponding to the reduced surface tension.

Second, good wetting is obtained more easily when the air surrounding the slide is saturated with water vapor to reduce evaporation along the line of contact of air, liquid, and glass. Third, it was found that a zero angle of contact could be obtained more easily if the slide is *raised through the surface* (receding contact angle) rather than lowered into it. This is particularly true when a film covers the water surface since the former procedure ensures contact between a fresh glass surface and the water surface while the latter favors contamination of the glass by the surface film. Thus, the slide should always *rise* to an equilibrium position as is the case in the continuous compression of a surface film before collapse. Oscillations of the slide during a force–area run should be avoided. The existence of a zero contact angle usually can be ascertained by visual inspection of the meniscus.

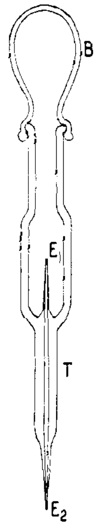

Fig. 2.—Automatic micro-volume pipet. The liquid to be delivered is held by capillary action between the fine capillary tips, E_1 and E_2.

Results

The results of a comparison of the film balance and the surface tension balance for the measurement of the surface pressure of a film of commercial lecithin on 0.001 N hydrochloric acid at 23° are given in Table I and Fig. 3. Here $-\Delta\gamma_{FB}$ represents the surface pressure measured by the film balance while $-\Delta\gamma_w$ is the surface pressure determined by the Wilhelmy balance.

To check the relative precision of the two

TABLE I

COMPARISON OF WILHELMY METHOD WITH FILM BALANCE FOR THE DETERMINATION OF SURFACE PRESSURES OF FILM OF COMMERCIAL LECITHIN ON 0.001 N HCl AT 23°. FILM PRESSURES IN DYNES PER CM.

Area per molecule, sq. Å.	$-\Delta\gamma_{FB}$	$-\Delta\gamma_{W}$	Diff. dynes./cm.	Area per molecule, sq. Å.	$-\Delta\gamma_{FB}$	$-\Delta\gamma_{W}$	% diff.
124.4	0.06	0.20	−0.14	71.07	10.95	10.88	0.6
107.4	.06	.20	− .14	66.80	15.65	15.38	1.7
92.40	.27	.30	− .03	62.55	21.76	21.63	0.6
88.20	1.42	1.29	+ .13	58.25	30.00	29.70	1.0
			% Diff.	54.00	35.00	34.68	0.9
83.85	2.90	2.81	3.1	49.72	37.72	37.40	.9
79.60	4.93	4.86	1.4	45.46	37.95	37.50	1.2
75.35	7.48	7.46	0.3		Collapse		

methods a simultaneous force–area run was made on a film of pentadecylic acid spread on 0.01 N hydrochloric acid. In this experiment the area per molecule was decreased by 0.5 sq. Å. every two minutes from below the limiting area at zero pressure to collapse. The surface pressure was determined by each method thirty and ninety seconds after each compression. The results are indicated in Fig. 4 and in Table II where a statistical analysis is given.

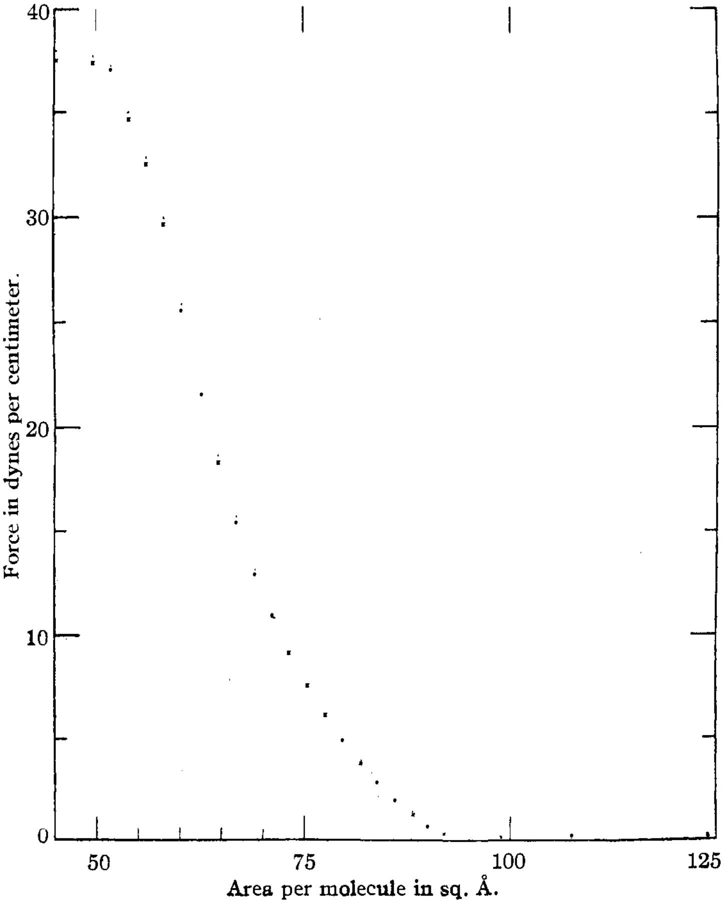

Fig. 3.—Force–area curve of a film of commercial lecithin on 0.001 N hydrochloric acid. Crosses indicate pressures determined by Wilhelmy balance while dots indicate pressures determined with film balance.

TABLE II

STATISTICAL COMPARISON OF RESULTS OBTAINED BY THE WILHELMY METHOD AND THE FILM BALANCE FOR A FILM OF PENTADECYLIC ACID ON 0.01 N HCl

Region of pressures, dynes/cm.	No. points	Mean diff. between pressures	Mean deviation from mean diff.	Remarks
0.1 to 3.2	20	0.04 dynes/cm.	0.03 dynes/cm.	
3.4 to 6.9	30	3.0%	.5%	
7.0 to 12.0	35	3.2%	.3%	Slow collapse
12.1 to 30.0	21	2.4%	.6%	of film

Table III A gives a comparison of the two methods for the relatively solid film which stearic acid forms on 0.001 f sodium bicarbonate at pH 8.2, while the results for the extremely rigid film of calcium stearate which it forms[10] on 0.0001 M calcium chloride at pH 8.8 are given in Table III B (see Fig. 5).

The agreement between the two methods is within the experimental errors both for the expanded films of lecithin and pentadecylic acid and for the very rigid films of stearic acid and calcium stearate. The pressures obtained by the film balance are consistently higher for pressures above 1 dyne/cm. for all the films studied. This small consistent difference may be due to errors made in the calibration of the film balance. Thus from Table II it is seen that the surface pressures of pentadecylic acid measured by the film balance are on an average 3.2% greater than those determined by the Wilhelmy method with a mean deviation from the mean per cent. difference of only 0.3% for pressures below collapse. After collapse begins the observed pressures become more nearly equal. This is due to the fact that as the film collapses the microscope slide sinks into the water and the contact angle is no longer zero. The result of poor wetting is an apparent increase in surface pressure since the surface tension then pulls on the slide with a smaller force than it would if ϑ were zero. The difficulty could be eliminated by compressing the film continuously since then the slide would constantly rise and give the receding contact angle.

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[10] I. Langmuir and V. J. Schaefer, THIS JOURNAL, **58**, 284 (1936).

A close inspection of Fig. 4, the force–area curve for pentadecylic acid, indicates that the pressures determined by the Wilhelmy method lie somewhat closer to a smooth curve than do those determined with the film balance. The larger part of the random deviation is thus probably due to the inaccuracies of the film balance.

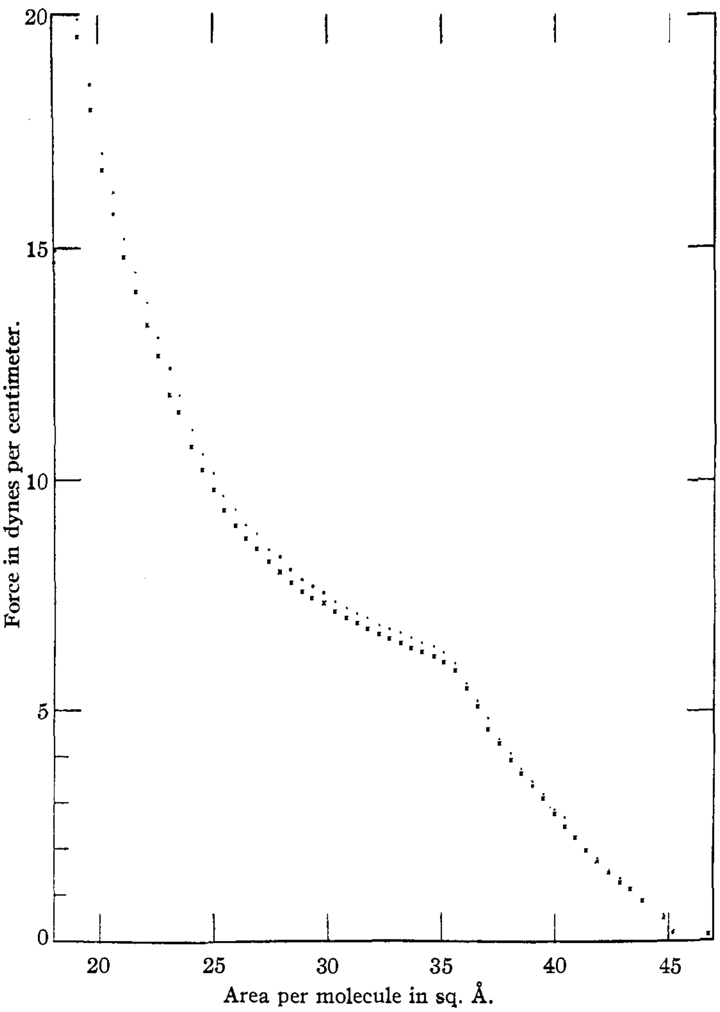

Fig. 4.—Force–area curve for pentadecylic acid on 0.01 *N* hydrochloric acid. Crosses indicate pressures determined by Wilhelmy method while dots indicate pressures determined by film balance.

Compression of Films of Stearic Acid by Calcium Ion

This preliminary work on the effects of hydrogen ion concentration and of bivalent positive ions has given results of importance for the area occupied in a film by a long hydrocarbon chain. On 0.01 *N* hydrochloric acid stearic acid forms a liquid expanded film of high compressibility at low pressures. At high pressures the film is liquid but condensed and has a moderately low compressibility. At 25° these straight lines extrapolate to 23.8 sq. Å. for the expanded film, and 20.4 sq. Å. for the condensed film at zero pressure.

Figure 5 shows that at 24.5° on 0.001 formal sodium bicarbonate at a *p*H of 8.2 the expanded part of the film persists, but that on compression the pressure does not begin to rise until just below 20.5 sq. Å. per molecule. The film becomes condensed at a pressure of 10 dynes per cm. and an area of 19.35 sq. Å. per molecule. This film may contain minute amounts of tin from the block tin condenser used in condensing the water, and of calcium in the "c. p." sodium bicarbonate used. Chromium, copper, and zinc from the brass trough also may have been present, although the film removed from the water surface with filter paper after each experiment was white.

TABLE III

COMPARISON OF WILHELMY METHOD WITH FILM BALANCE FOR THE DETERMINATION OF SURFACE PRESSURES OF STEARIC ACID FILMS. FILM PRESSURE IN DYNES/CM.

Area per molecule, sq. Å.	$-\Delta\gamma_{FB}$	$-\Delta\gamma_W$	Diff. dynes/cm.	Area per molecule, sq. Å.	$-\Delta\gamma_{FB}$	$-\Delta\gamma_W$	% diff.
A. On 0.001 *M* $NaHCO_3$; *p*H 8.2 at 24.5°							
29.80	0.14	0.20	−0.06	19.59	5.72	5.65	1.2
23.05	.17	.25	− .08	19.41	7.54	7.38	2.1
21.37	.21	.29	− .08	19.25	10.18	10.12	0.6
20.93	.26	.31	− .05	19.08	15.35	15.17	1.2
20.51	.37	.40	− .03	18.91	21.46	21.30	0.8
			% Diff.	18.74	...	28.73	...
20.10	1.60	1.61	− 0.6	18.57	35.73	35.65	0.2
19.92	2.65	2.67	− .8	18.40	42.03	41.30	.6
19.75	4.20	4.15	1.2	18.24	Collapse		
B. On 0.001 *M* $NaHCO_3$, 0.0001 *M* $CaCl_2$ + NaOH; *p*H = 8.8 at 22.7°							
			dynes/cm.				
44.13	0.04	0.05	−0.01	19.45	15.67	15.36	2.0
24.53	.10	.05	+ .05	19.28	25.90	25.72	0.7
22.19	.10	.08	.02	19.15	34.90	34.77	.4
20.63	.21	.11	.10	19.06	33.20	33.17	.1
19.84	.30	.21	.09		Collapse		

The compressibility[11] of this film is 0.00132 cm. dyne^{-1}, and before collapse the film becomes compressed at 42 dynes per cm. to 18.4 sq. Å. the lowest area as yet found in films for a long hydrocarbon chain.

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[11] The compressibility C_F of a two dimensional film is defined by the equation

$$C_F = \frac{(a_1 - a_2)/a_1}{\gamma_2 - \gamma_1}$$

where a_1 is the area per molecule corresponding to the surface tension γ_1 before compression and a_2 is the area per molecule corresponding to the reduced surface tension γ_2 after compression.

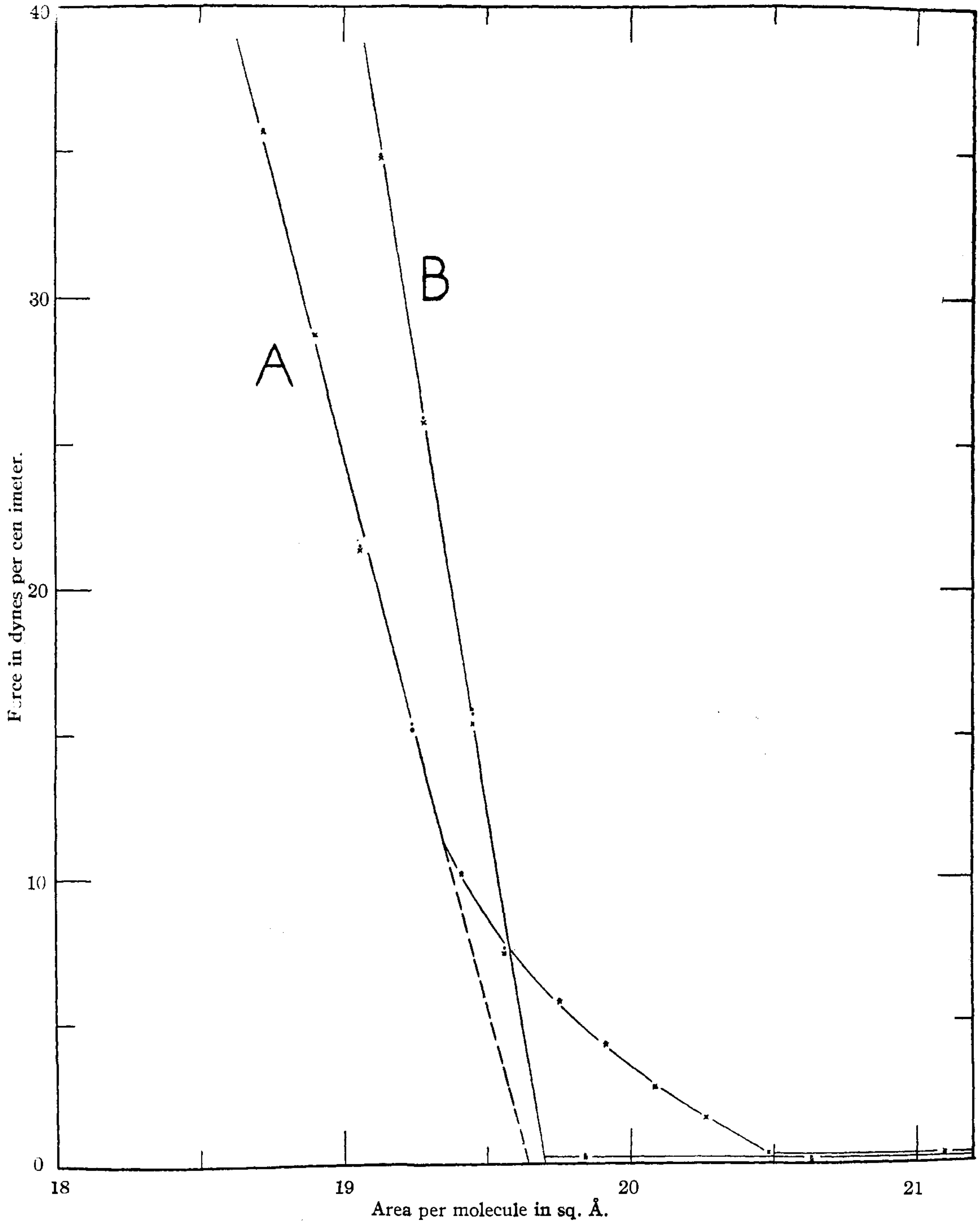

Fig. 5.—Effect of calcium ion on stearic acid films: A, force–area curve of stearic acid on 0.001 *f* $NaHCO_3$, *p*H 8.2 at 24.5°; B, force–area curve of stearic acid on 0.001 *f* $NaHCO_3$, 0.0001 *f* $CaCl_2$ + NaOH; *p*H 8.8 at 22.7°. Crosses indicate pressures determined by Wilhelmy method while dots indicate pressures determined with film balance.

When the sodium bicarbonate is made 0.0001 *f* in calcium ion a marked change occurs. The expanded part of the curve disappears and the area at zero pressure becomes 19.70 sq. Å. per molecule which is the same within the experimental error as the extrapolated value (19.64) obtained from the condensed film without the calcium. The calcium stearate film exhibits an extremely low compressibility (0.00081 cm. dyne^{-1}).

The extremely low values for the molecular areas found in this work indicate a very tight packing of the hydrocarbon chains in the film. The lowest previously accepted value is 20 sq. Å. The value of 18.4 sq. Å. obtained here is almost the lowest which can be obtained by the close packing (as in hexagonal close packing) of hydrocarbon chains.

Summary

It is found that a film balance of great simplicity of construction and operation, and of high accuracy, is obtained by the use of the Wilhelmy method for the determination of surface tension in a proper differential form. Since the differential method thus developed makes use of the balance between a vertical pull of the surface tension directed downward, and the vertical upward force of buoyancy of the liquid, this may be considered as a vertical-pull method, as distinguished from the ordinary horizontal-pull film balance now in general use. While the method is suitable for investigations of the highest accuracy, its great simplicity makes it particularly suitable for biological and industrial work. The apparatus has the following additional advantages. (1) It can be built easily so that only quartz, or some other suitable material, comes in contact with the water. This makes it easy to investigate the effect of minute quantities of metal ions, while with the ordinary film balance this is very difficult. (2) It is suitable for a study of the effect of the rate of continuous compression of a film. (3) Its operation is very rapid, and easily may be made entirely automatic.

The effects of calcium ion on the films of stearic acid have been studied. Without the addition of this ion, the acid on 0.001 *f* sodium bicarbonate at 24.5° forms an expanded film with a limiting area of 20.5 sq. Å. per molecule, and this is converted into a condensed film at 10 dynes per cm. The extrapolated limiting area of this condensed region (19.70 ± 0.08 sq. Å. per molecule at zero pressure) is the same as the actual limiting area of the extremely condensed film which stearic acid forms on the same buffer made 0.0001 *f* in calcium chloride. Thus Ca^{++} ion compresses the fatty acid ions of the film, and eliminates the expanded region obtained without it.

The mathematical theory of the ordinary "horizontal-pull" film balance is developed, and data are presented which show that the two types of film balance give essentially the same values of the surface pressure with either liquid or solid films, even if the latter are extremely rigid.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND BAKER CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

The Surface Tension of Aqueous Soap Solutions as a Function of Hydrogen Ion (*p*H) and Salt Concentration. I. Sodium Laurate and Sodium Nonylate

BY F. A. LONG, G. C. NUTTING AND WILLIAM D. HARKINS

1. Introduction

This investigation was undertaken as a preliminary to a study of the effects of hydrogen ion and salt concentration upon the surface tension of biological liquids. These effects are extremely great in soap solutions, as was shown for solutions of sodium oleate by Harkins and Clark and by Powney.[1] Solutions of soaps alone have been found to exhibit very low surface tensions at very small concentrations[2] and this was explained by Harkins and Clark as due to the fact that the acid formed by the hydrolysis of the soap is very much more highly adsorbed than the soap itself: that is, than the negative paraffin chain ion plus electrostatically held positive metal ion.

Soap solutions are of particular interest on account of the presence in them of a considerable number of paraffin ion micelles above a certain critical concentration, which is low if the paraffin chain is long.[3] Since this critical concentration seems to lie in the region of rapid change of surface tension with soap concentration, an

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[1] William D. Harkins and G. L. Clark, THIS JOURNAL, **47**, 1854 (1925); J. Powney, *Trans. Faraday Soc.*, **31**, 1510 (1935).

[2] William D. Harkins, G. L. Clark, E. C. H. Davies, THIS JOURNAL, **39**, 541 (1917); E. E. Walker, *J. Chem. Soc.*, **119**, 1521 (1921); L. Lascaray, *Kolloid-Z.*, **34**, 73 (1924); A. Lottermoser and W. Tesch, *Kolloid-Beihefte*, **34**, 339 (1931).

[3] G. S. Hartley, "Aqueous Solutions of Paraffin Chain Salts," "Actualites Scientifiques et Industrielles, "Paris, 1936. See also papers by McBain.