ductances were determined at 25°. The function $L_3 - L_2 = ac_3 - bc_3 (\mu_v^{1/2} - c_2^{0^{1/2}})$ was proposed to represent the experimental data. The constants of the equation were determined by the method of least squares and were found to predict the observed values with an average deviation of 0.01%.

SEATTLE, WASHINGTON RECEIVED DECEMBER 21, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A Comparative Study of Surfaces of Solutions with the Film Balance and Surface Tension Equipment

BY JAMES W. MCBAIN AND EVERT R. SHARP*

When the film balance is applied to the study of uncontaminated solutions,[1] results are obtained which could not have been anticipated from studies of insoluble films or from the ordinary theory of diffusion. It is therefore very important to find out whether these complicated surface effects are paralleled by corresponding changes in surface tension as measured by other standard equipment.

The nearest instrument to the film balance is the PLAWM trough[2] which has an impermeable flexible partition between the liquids on the two sides of the floating barrier and thus actually measures surface tension on plane swept surfaces. Wilson[2,3] had already shown that this gave results closely similar to that of the Lloyd and Scarth ring method. Thus, although all experiments with the film balance can be paralleled by more complete measurements with the PLAWM trough, it is experimentally much easier to use the film balance and the duNoüy tensiometer, or ring method.

The ring method has been criticized as referring to surfaces that are not completely static or undisturbed. However, this disability may be obviated by using the ring on a very large swept surface, such as that in the film balance or PLAWM trough, for then the disturbance involves a negligible proportion of the surface. The same consideration applies to the Wilhelmy method. The remaining objection that the solution lying within the ring is more extensively disturbed and therefore may inject some doubt into the measurements, is likewise obviated if two rings of different diameter are used and yet give the same result. For our purpose only the first precaution was necessary to establish what it is that is observed in the film balance.

We have found that the changing pressures observed on compressing and expanding the superficial areas of solutions in the film balance are paralleled by changes in surface tension found with the duNoüy tensiometer on the same large surfaces.

The Film Balance

The equipment and precautions described by Spencer[1] were again employed, but the whole apparatus was placed inside a new air-tight metal cabinet of practically saturated humidity, with glass front and sliding glass doors for use during actual manipulation. The double walls were six inches thick on four sides, and were filled with water thermostated at 25°. The platinum–iridium float was provided with short platinum wires coated with dicetane to which the suspending threads were tied.

This cabinet also contained for use with the tensiometer a fused silica trough 38 cm. long and 15 cm. wide, with six coats of Bakelite lacquer. This was mounted on a disk with three levelling screws. The disk was mounted on a stand with micrometer screw to raise and lower the tray. The area available for sweeping was 450 sq. cm. The 0.25 mm. steel torsion wire was thinly coated with Bakelite lacquer. The 40 mm. platinum ring was always washed and heated to redness before use. The surface tension of pure water after calibration of the wire appeared as 72.00 dynes/cm. as compared with the standard value 71.97.

Invariably, sweeping[1] and tests for contamination[1] preceded each experiment.

The nine procedures of previous studies[4] with the film balance were simplified to four for use with the tensiometer trough. These should be briefly recorded. Force–area curves are illusory when obtained with soluble surfaces.

Procedure I_a determines the rate at which surface tension attains equilibrium, and also the maximum observable change of surface tension between a freshly swept and a completely aged surface. After repeated sweeping, *away from* the float or from the very end of the trough, the initial surface tension is taken as rapidly as possible and then at

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* Thesis (87 pages, including 21 figures and 34 tables) available in bibliofilm through the Department of Agriculture, Washington, D. C.

(1) References to eight papers by Doss, 1935–1939, and to four papers from this Laboratory, 1935–1939, are given in McBain and Spencer, THIS JOURNAL, **62**, 239 (1940).

(2) McBain, Vinograd and Wilson, *ibid.*, **62**, 244 (1940).

(3) McBain, Ford and Wilson, *Kolloid-Z.*, **78**, 1 (1937).

(4) McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939).

definite time intervals until no further change can be observed. This may require several thousand minutes for some solutions, and no interval at all for others. The latter are described by Perry and Spencer as instantly reversible.

Procedure II$_s$ measures changes in surface tension on compressed surfaces. At a definite time or age after sweeping, the surface is compressed by a definite amount, such as 75%, by moving the barrier three-quarters of the way *toward* the float or the end of the trough. The surface tension is measured before and after and then at intervals until constant. The whole is repeated at a series of different ages and compressions.

Procedure III$_s$ measures the amount by which a surface may be compressed in order to cause (a) an observable change in surface tension and (b) a temporary film or (c) a permanent pellicle on the surface. After sweeping, and taking the surface tension at any definite age from 0 to several days, the barrier is *slowly* moved *toward* the float and the surface tensions recorded.

Procedure IV$_s$ focusses attention upon the pellicle, if any, and measures its final characteristic value below which it cannot dissolve. After sweeping and then aging, the surface tension is taken and then the surface compressed by, say, 87.5%, and the surface tensions taken until constant.

Experiments with Hydrocinnamic Acid

Film Balance.—Experiments of Perry and Spencer were repeated in the film balance with 1 g. of recrystallized Eastman Kodak Co. acid per liter, confirming that the pressure difference caused by sweeping the solution amounted to 0.41 dyne/cm. in thirty minutes after stopping the sweeping (Perry 0.41, Spencer 0.40), rising to 1.60 in 1500 minutes (Spencer 2.17 in 4000 minutes). This is almost infinitely slower than the fraction of a second calculated from ordinary diffusion theory, but it agrees with the observation of McBain, Ford and Mills[5] that the surface tension is not established for at least a day.

As a consequence it follows that the values obtained by compressing the surface must depend upon whether the previous aging was only thirty minutes, as used by Perry and Spencer, or much longer. For age thirty minutes, compression yields initial pressures of as much as 4 dynes/cm. which gradually fall to a final constant value of 0.41 (Perry 0.42, Spencer 0.42). The first noticeable effect of compression was at 12.5%. However, if the surface is more fully aged before compression, the initial and final pressures produced by compression are several times larger.

Tensiometer.—In Procedure I$_s$ the difference in surface tension between an aging and a continually swept surface became constant at 1.7 dynes in 800 minutes, tested for 2000 minutes, in agreement with the value 1.60 dynes obtained with the film balance, 1500–1800 minutes. The curve for Procedure I$_s$ is shown in Fig. 1. The tensiometer is of course less sensitive than the film balance.

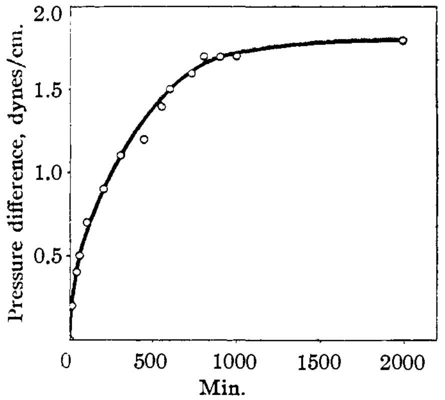

Fig. 1.

The results of Procedure II$_s$ are given in Table I for 75% compression, and for solutions up to thirty minutes after sweeping. The initial pressure in the table is obtained by subtracting the surface tension just after compression, column 3, from that just before compression, column 2. Similarly the last column is obtained by subtracting column 4 from column 2. The film balance which measures only differences gave for initial pressure for surface aged thirty minutes before compression, 1.69, and after ten minutes 1.28 dynes/cm. in agreement with the tensiometer.

TABLE I

TENSIOMETER PROCEDURE II$_s$ SHOWING SURFACE TENSIONS OF HYDROCINNAMIC ACID SOLUTIONS (1 G./LITER) BEFORE AND AFTER COMPRESSION AND TEN MINUTES LATER

Aging, min.	Before Compression	After Compression	10 min. thereafter	Difference Initial	Difference 10 min.
1	67.8	67.7	67.8	0.1	0
5	67.7	67.3	67.7	0.4	0
15	67.6	66.7	67.2	0.9	0.4
20	67.5	66.4	66.7	1.1	0.8
30	67.4	65.8	66.1	1.6	1.3

Procedure III$_s$ again agrees with the film balance if allowance is made for the lower sensitivity and slowness of measurement of the tensiometer as compared with the film balance. Table II refers to a solution aged thirty minutes after sweeping whose surface tension before the slow successive compressions was 67.4 dynes/cm. The

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[5] THIS JOURNAL, 62, 1319 (1940); see also the similar time effects assembled by McBain, Vinograd and Wilson, reference 2.

pressures are obtained by subtracting the surface tensions from this value. The values in the last column are taken from a completely independent experiment with the film balance. The final surface tension value after 87.5% compression rose to 66.9, thus leaving a final pressure of 0.5, whereas the film balance gave 0.41 dyne/cm.

Table II

Tensiometer Procedure III_s, Showing Surface Tension Changes of Hydrocinnamic Acid Solution Caused by Progressive Compression

Compression %	Initial dynes/cm.	Initial pressure	Film balance
12½	67.3	0.1	0.06
25	67.3	.1	.21
45	67.0	.4	.57
50	67.0	.4	.66
75	66.1	1.3	1.85
80	65.8	1.6	2.31
87½	64.0	3.4	3.21

Procedure IV_s is represented in Figs. 2 and 3.

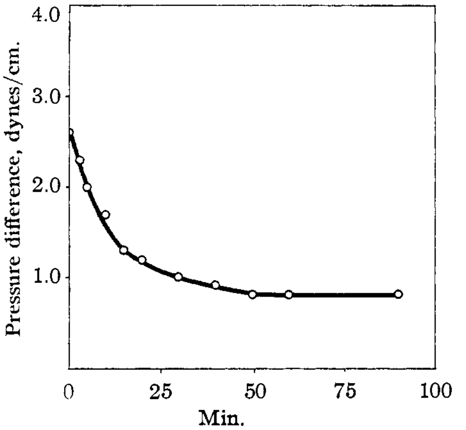

Fig. 2.

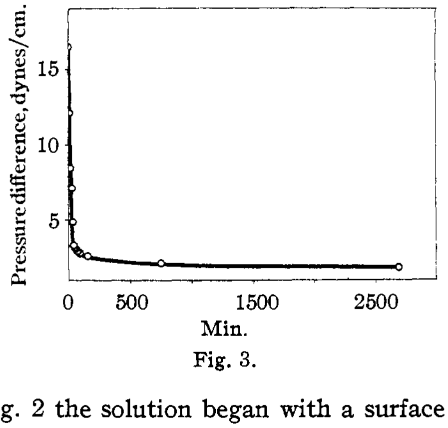

Fig. 3.

In Fig. 2 the solution began with a surface compressed 87.5% just thirty minutes after sweeping, whereas in Fig. 3, it was fully aged; that is, 2000 min. after sweeping before the 87.5% compression. In the first instance the surface tension before compression was 67.4 and in the second instance 64.0 dynes/cm. In Fig. 3 with a fully aged surface the final surface pressure was 1.8 dynes/cm. at 2680 min. after compression. This is the true "final characteristic value." The "final characteristic value" obtained by Perry and Spencer was for solutions aged thirty minutes before compression for which with film balance we again get in agreement with them, 0.42, 0.41 and 0.41 dyne/cm. in three separate experiments, the initial pressure produced by compression being about 3.8.

In tensiometer Procedure IV_s carried out on a surface aged only thirty minutes after sweeping, comparison is naturally made with the unchanging value 67.4 dynes/cm. In the film balance, however, the surface of comparison itself continues to age. Hence in the tensiometer experiments the final pressure difference of 0.8 dyne/cm. observed in Fig. 2 should be corrected by comparing it with the surface tension of a solution about one-hundred minutes old as given in Procedure I_s. Thus $67.1 - 66.6 = 0.5$ dyne/cm. final pressure, as would be observed in the film balance.

It is not surprising that pressure differences observed with clean solutions with the film balance should prove to be differences of surface tension on the two sides of the float, for Miss Agnes Pockels invented the film trough for making measurements of surface tension on both sides of the float, and Langmuir replaced this procedure by measurement of the difference in tension or pressure on the float. Alexander and Theorell[6] for insoluble interfacial films between liquids showed that a film balance gave results in accord with the tensiometer.

Alexander[7] has recently reviewed and extended the experimental evidence on aging of solutions found by ourselves and many other authors. He states, "With hydrocinnamic acid examination by the dark-field ultramicroscope of the surfaces of aged solutions showed that micro-crystalline aggregates were formed on compression. This readily explains the difference between fresh and aged surfaces for the spreading of oils and also many of the other phenomena observed by McBain and his co-workers." This would appear to be direct evidence for our pellicle, but curiously the author

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(6) Alexander and Theorell, *Trans. Faraday Soc.*, **35**, 727 (1939).

(7) Alexander, *ibid.*, **37**, 23 (1941).

thinks otherwise. He also fails to provide a satisfactory theory of these phenomena.

Solutions of Mono-sodium Sulfonate of Dioctyl Succinate.—This substance is available in chemically pure form and is best known as "Aerosol OT." We have investigated three very dilute solutions with the tensiometer. The results are illustrated by Figs. 4 to 8, and Procedure I_s is briefly summarized in Table III; Fig. 5 shows these results in more detail. The static surface tensions of the fully aged surfaces are given in Table III, together with the time after sweeping required to attain them. These may be compared with Fig. 4 which gives results of ordinary tensiometer measurements by Ts-Ming Woo and H. D. Bruce at 25°.

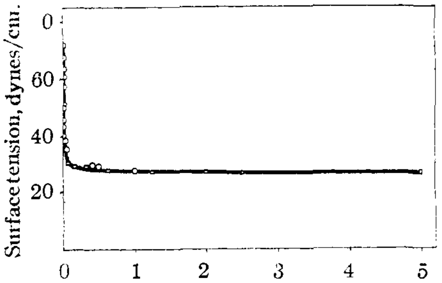

Fig. 4.

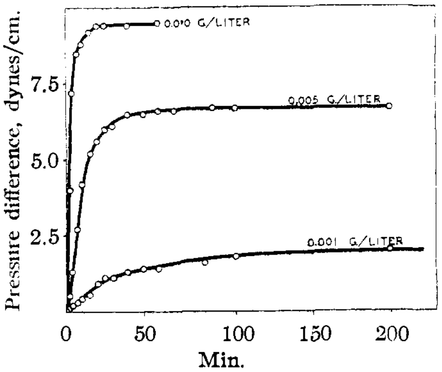

Fig. 5.

TABLE III

Surface Tension of Solutions of Aerosol OT (Procedure I_s) Showing Effect of Sweeping and the Time Required for Recovery

Concn. g./liter	Maximum pressure dynes/cm.	Static surface tension	Min. required
0.001	2.9	67.66	1080
0.005	6.7	63.5	85
0.010	9.5	59.70	20

Procedure IV_s was carried out in installments, first compression being to 25% and then from there after complete aging to 50%, and similarly in two further steps to 75 and 87.5%. A very remarkable result immediately appears. In every case there is a maximum final pressure of the pellicle when the compression is 75%. Further compression renders the pellicle for some reason more readily soluble. This is in complete contrast to hydrocinnamic acid. With it the final pressure supported by the pellicle, which must be exceeded to dissolve it, remains constant for all higher compressions. If the pellicle is a polymolecular film, then in the case of Aerosol OT it must buckle and expose soluble groups. Both initial and final pressures of its pellicle are greatest at 75% compression.

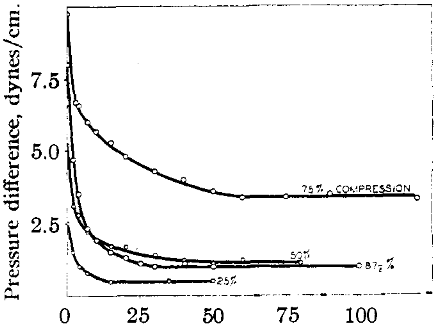

Fig. 6.

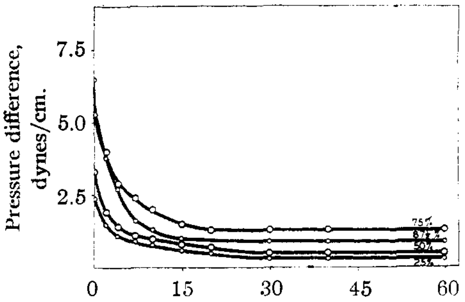

Fig. 7.

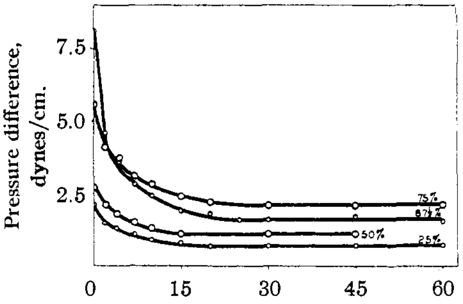

Fig. 8.

Results of Procedure IV_s are given in Figs. 6–8. The pressure differences plotted are obtained by subtracting the surface tension at any moment from the final static surface tension given in Table III. The longest interval for the initial pressure to fall to the final pressure was seventy-five minutes observed for the most dilute solution with 75% compression. The shortest was fifteen minutes observed with the same and several other solutions at low compression.

An Experiment with Potassium Chloride

Jones and Ray[8] found a minimum in the surface tension of 0.001 *m* potassium chloride. This minimum has been variously ascribed to methodical error or explained by *post hoc* theories with or without retaining the applicability of the Gibbs theorem. Dole and Swartout[9] have apparently verified its existence. In the film balance sweeping away from the float produces no effect. However, compression to within 87.5% of the float produced an initial pressure of 0.15 dyne/cm. which fell off in ten minutes to zero. Repetition here by F. Van Acker, Jr., appears to substantiate these results. Hence there would appear to be positive adsorption at this minimum. The microtome method with far more concentrated solutions of sodium chloride showed negative adsorption.[10]

Surface Tension of Sodium Silicate

It is of interest to record the surface tension of a sodium silicate solution since practically no data are available. The Philadelphia Quartz Company supplied some "N" brand containing 28.37% SiO_2 and 8.87% Na_2O, ratio 3.19. This shows a curve somewhat similar in form to that of potassium chloride, but on a different scale, and with an unusual time effect. There is a small but distinct minimum in surface tension for a concentration containing 2 g. of silicate (0.580 g. SiO_2) per 100 cc. Above 5% the surface tension rises steadily above that of water. The curve is shown in Fig. 9. It is quite unusual that in the neighborhood of the minimum the surface tension rises with time instead of falling to the static value. A parallel result was obtained by Mr. H. B. Bruce using other equipment. However, with "BW" brand (31.98% SiO_2 and 19.60% Na_2O, ratio 1.63) the surface tension gave no definite indication of a minimum and rose about twice as fast with concentration. All these silicate solutions are of course too complicated to have unambiguous theoretical significance.

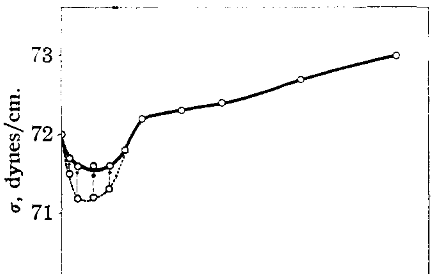

Fig. 9.

Summary

1. It has been shown for the surface of solutions of hydrocinnamic acid that the complicated phenomena discovered with the film balance are paralleled by changes in surface tension observed on similar surfaces with the tensiometer or ring method. They are, however, more readily studied with the film balance.

2. Instead of only the fraction of a second predicted from simple diffusion, surfaces of solutions of hydrocinnamic acid require one or two thousand minutes to arrive at their steady surface tension.

3. When the surfaces of solutions of hydrocinnamic acid or of Aerosol OT are suitably reduced in area, a pellicle is formed which will not dissolve unless a definite pressure is exceeded. For dilute solutions of Aerosol OT this pressure is at a maximum for a surface 75% compressed.

4. Observations were also made with potassium chloride and sodium silicate. With $N/1000$ potassium chloride solution compression of the surface appears to produce a temporary surface pressure.

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RECEIVED JANUARY 23, 1941

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(8) Jones and Ray, THIS JOURNAL, **59**, 187 (1937).

(9) Dole and Swartout, *ibid.*, **62**, 3039 (1940).

(10) McBain and Swain, *Proc. Roy. Soc.* (London), **154A**, 608 (1936).