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Studies of Solutions of Hydrocinnamic Acid and of Lauryl Sulfonic Acid with the Film Balance

BY JAMES W. MCBAIN AND WARREN V. SPENCER

In 1935 McBain and Wilson¹ and Doss² showed that the Pockels–Langmuir–Adam trough or film balance invented for insoluble films floating on water, gave highly interesting and unexpected results when applied to clean surfaces of ordinary solutions. The film balance does not measure surface tension of solutions. It has, however, uncovered the fact that while some solutions may have their surfaces enlarged by sweeping, or contracted by compressing with a movable barrier, without in any way affecting the balance or float, others are very sensitive to one or the other or both of these procedures. Often different behavior depends upon the range of concentration of one particular substance, and all the phenomena may go through maxima in intermediate concentration.

Two of the most striking phenomena are, first, the long times, almost infinitely long as compared with processes of diffusion, that are involved in some instances, and not in others or in other concentrations; and, second, the discovery of the formation of a semi-insoluble pellicle upon suitable compression of certain surfaces, exhibiting a well-defined "characteristic final pressure," at or above which only it will dissolve. A simple example of this behavior is normal caproic acid in aqueous solution, one of the most stable com-

pounds of organic chemistry. McBain and Perry¹ ascribed this to orientation.

The phenomena are so novel and complicated that no satisfactory explanation embracing all of them has yet been forthcoming. They are not due to contamination, or to evaporation, for these have been painstakingly avoided, at least in the later work.

Doss considers that diffusion in the surface zone of a solution has to be activated and suggests that a potential barrier is formed by the diffuse double layer. He suggested that if the concentration is doubled the rate of accumulation in the surface should increase more than fourfold. However, we here find for solutions of lauryl sulfonic acid, proceeding from a concentration of 1.55 g./liter, that the velocity is increased either by concentration or by dilution.

To account for the special properties of the pellicle McBain and Perry suggest formation of polymolecular leaflets with the hydrophilic groups not exposed.

The present communication describes experiments upon several specimens of hydrocinnamic acid, cinnamic acid and, most carefully, dodecyl sulfonic acid, the latter being an example of the very large group of modern detergents with Type III curves of surface tension.³ In these a mere trace lowers the surface tension of water by a large fraction. Upon further addition the sur-

(1) McBain and Wilson, *THIS JOURNAL*, **58**, 379 (1936); see also McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939).

(2) Doss, *Current Sci.*, **4**, 405 (1935); see also *ibid.*, **5**, 645 (1937); **6**, 446 (1938); **7**, 182 (1939); *Proc. Indian Acad. Sci.*, **4**, 11, 97 (1936); *Kolloid Z.*, **84**, 138 (1938); **86**, 205; **87**, 272 (1939).

(3) McBain, Ford and Wilson, *Kolloid Z.*, **76**, 1 (1937); McBain, Vinograd and Wilson, *THIS JOURNAL*, **62**, 244 (1940).

face tension either remains constant or, as in this case, actually rises again. The most concentrated solution studied was only 5 g./liter and the minimum in the surface tension curve lies at 1.55 g./liter.

Apparatus and Method

A Cenco film balance was remodelled. The trough was coated with twenty-five superimposed layers of bakelite lacquer, each baked on for thirty minutes at 135–150°. The level of the liquid was fixed by a capillary tube attached to a suction pump near the end of the trough. The trough was 14 cm. wide and the barrier was always placed originally 40 cm. from the float. For solutions of lauryl sulfonic acid a thin coat of dicetyl was placed on the edges of the trough and the level of the solution kept low.

The float was a strip of platinum-iridium bent longitudinally to form an inverted V, the top of the fold coated with dicetyl and the bottom dipping deeply into the solution. Dicetyl was used with 0.0025 mm. gold foil to make the connection between float and trough. Before assembling, the float was heated to redness. The torsion wire was non-rusting 0.18 mm. phosphor-bronze used within its elastic limit. The barriers were of fused silica 1 cm. square and 26 cm. long, completely coated with bakelite lacquer, with some dicetyl where they touched the edges of the trough when using lauryl sulfonic acid.

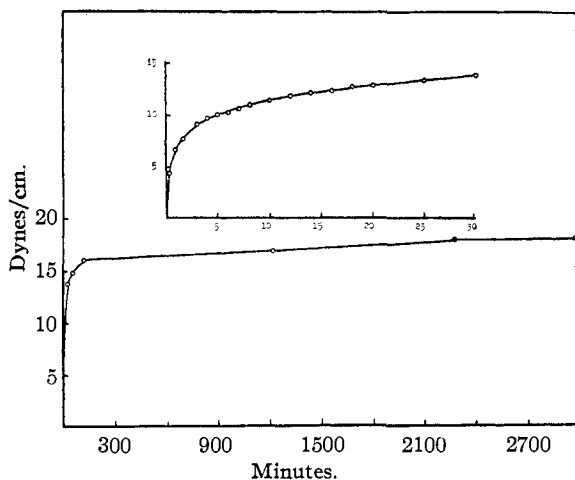


Fig. 1.—Laurylsulfonic acid 1.55 g. per liter, Procedure I.

To eliminate evaporation the entire trough was placed in a tight chamber thermostated at 25° using 42 ft. (12.8 meters) of 1/4" (6.4 mm.) copper tubing, through which thermostated water flowed. The bottom of the chamber was an open reservoir of thermostated water into which dipped cloth drapes to help keep the enclosed atmosphere saturated.

Invariably, before each experiment and procedure (except Procedure II), the surfaces on both sides of the float were swept several times by placing a barrier next to the float and sweeping it away. Each barrier in turn was left in place at the end of the trough until another had come back to it. The tests for contamination were described by

McBain and Perry. Pure water was always studied for several days before using any solution. If clean, neither sweeping nor compression nor time affects the position of the float.

The routine of operations, abbreviated from the procedures of McBain and Perry is¹ sweeping both sides to begin with, and continuing to sweep the large side, the torsion necessary to keep the float in the zero position is noted. Having thus measured both the maximum pressure difference and the time required for its production, these are confirmed by Procedure II, by the simple expedient of stopping the sweeping and measuring the rate and time for the pressure to fall to zero.

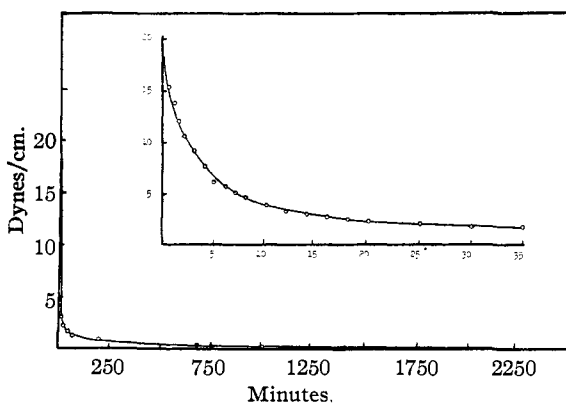


Fig. 2.—Laurylsulfonic acid, 1.55 g. per liter, Procedure II.

Again, both sides being swept and fully aged, the area on the large side is diminished by a definite percentage by moving the barrier toward the float and the initial and final pressure and the rate of change throughout are determined. Other procedures described by McBain and Perry occasionally were used.

Hydrocinnamic and Cinnamic Acids

Results with Eastman Hydrocinnamic Acid.—The hydrocinnamic acid was recrystallized from hot water and the principal results of McBain and Perry were repeated and confirmed. However, very much longer time effects were observed although the results show a close agreement with those of McBain and Perry for similar time intervals. For example, in Procedure I, after thirty minutes of aging, McBain and Perry found a pressure difference of 0.41 dyne per cm. while we now find 0.40, although in 4000 minutes this rises to 2.17 with a change of only 0.02 dyne during the last nineteen hours. In both Procedures I and II, the more rapid change has been accomplished within about five minutes. Classical diffusion phenomena would of course account for less than a second. These extremely slow adjustments are in accord with observations of surface tension of hydrocinnamic acid solutions communicated by McBain, Ford and Mills.⁴

Again, if the surface is compressed and then allowed to stand at constant area for a sufficiently long period, we obtain the same final characteristic pressure as McBain and Perry, namely, 0.42 dyne per cm. The first observable initial pressure occurs at 45% compression as was found by McBain and Perry.

(4) McBain, Ford and Mills, to be published.

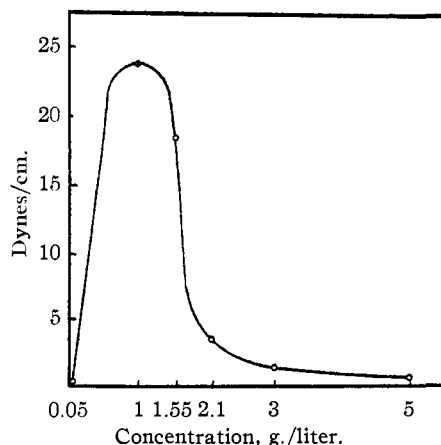


Fig. 3.—Laurylsulfonic acid, Procedure I. Maximum pressures produced on float by sweeping away from float.

Results with British Drug Houses Hydrocinnamic Acid.—The surface properties for all shorter times agreed with the foregoing, but for longer periods the values here were less. With 87.5% compression, the initial pressure for Eastman and British Drug Houses, respectively, was 2.4 and 2.5, falling in 30 min. to 1.18 and 1.15, and giving the final characteristic pressure after standing overnight 0.42 and 0.41.

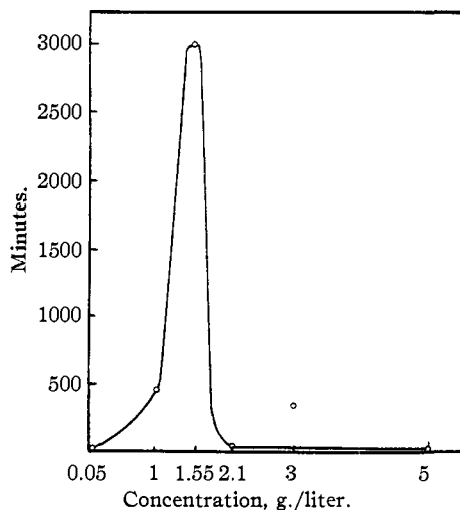


Fig. 4.—Laurylsulfonic acid, Procedure I. Time required for maximum pressure.

Experiments with Cinnamic Acid.—When 0.01 g. of cinnamic acid crystals was sprinkled on 560 sq. cm. of clean water, the spontaneous pressure after twenty minutes was 0.4 dynes/cm. falling off overnight to the final pressure of 0.19. Upon compression by 95%, the initial pressure became 1.03, but this fell to the 0.19 final value overnight.

Now when a solution of hydrocinnamic acid was similarly contaminated with cinnamic acid crystals, a maximum pressure of 2 was produced, which 87.5% compression raised to 3.33, falling to a final pressure overnight of

0.59 (= 0.41 + 0.18!). However, after thorough sweeping, apparently all cinnamic acid was eliminated, for on compressing surfaces aged thirty minutes by 87.5% the initial pressure was 2.5, falling in thirty minutes to 1.10 and giving the characteristic final pressure 0.40; all three values were thus identical with those quoted above for pure hydrocinnamic acid.

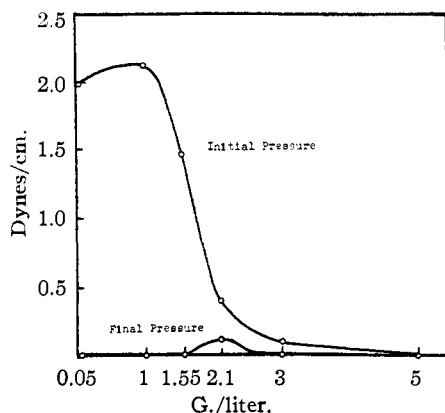


Fig. 5.—Laurylsulfonic acid, Procedure V, compressed 10%.

Spreading of Oil on Solutions of β -Phenylpropionic Acid.—Oil spreads upon a freshly swept solution extremely rapidly, just as on water,⁵ and the oil spreads circularly about as fast as the eye can follow. However, when the surface is aged and compressed, the oil again spreads circularly but very slowly. Freshly swept surfaces of solutions of hydrocinnamic acid are quite mobile while the compressed surface shows rigidity.

Similar experiments with oxidized oil and oleic acid were attempted on a solution of lauryl sulfonic acid of minimum surface tension containing 1.55 g./liter. On a freshly swept surface the drop rapidly spreads circularly until several centimeters in diameter. Then islands appear in the oil film which gradually breaks up into a very large number of minute droplets. On compressing and expanding the surface rapidly, these expand and the larger ones again form islands. On a clean aged surface the

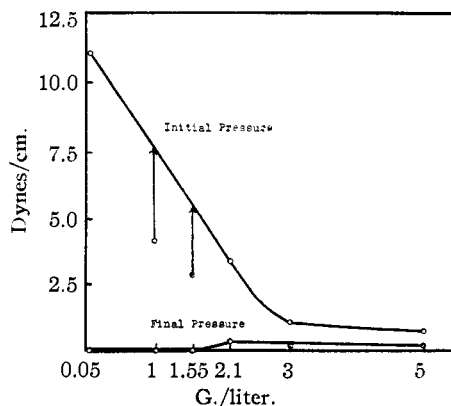


Fig. 6.—Laurylsulfonic acid, Procedure V, compressed 50%.

(5) T. F. Ford and D. A. Wilson, *J. Phys. Chem.*, **42**, 1051 (1938).

drops do not spread at all. Upon compression the surface moves as a whole, showing some elasticity.

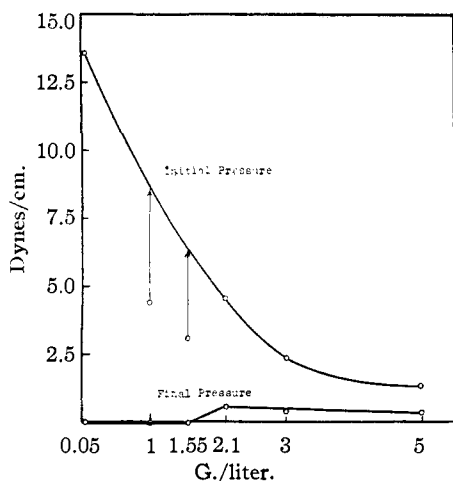


Fig. 7.—Laurylsulfonic acid, Procedure V, compressed 75%.

Dodecyl Sulfonic Acid

Study of Solutions of Dodecyl Sulfonic Acid. Five Grams per Liter.—Fifteen to twenty minutes are required before the effect of sweeping away from the float disappears and the maximum effect is 0.51 dyne per cm.

A pellicle is formed on sufficient compression. It is only after the surface has aged for the above-mentioned fifteen or twenty minutes that the final constant characteristic pressure of lauryl sulfonic acid of 0.51–0.52 dyne per cm. is exhibited upon compression and sufficient standing, then for 87.5% compression the initial pressure is 2.54, falling in about twenty min. to the 0.52 value. There is no initial pressure until compression amounts to 20% and no final pressure at all until the compression is 40%. The final pressure does not reach its characteristic constant value until the compression is 85% or more. The

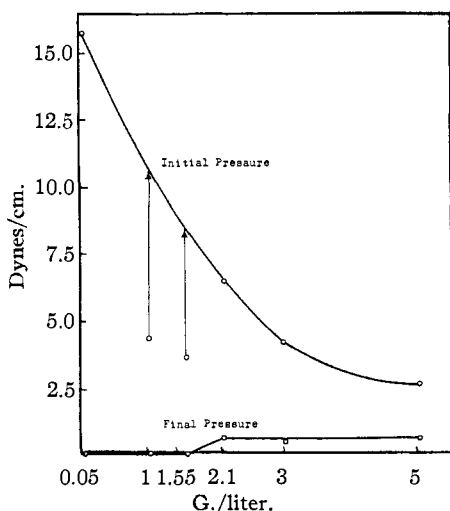


Fig. 8.—Laurylsulfonic acid, Procedure V, compressed 87½%.

time effects of compression are interesting and unexpected. Both for small and for very high compressions the fall to the characteristic pressure is rapid. For moderately large compressions, the time passes through a high maximum. This is observed again with other dilutions.

Three Grams per Liter.—Instead of the fifteen to twenty minutes above, six hours is here necessary for this solution to recover after sweeping away from the float, and the maximum effect is raised from the 0.51 to 1.34 dynes per cm. Compression again produces a pellicle.

2.1 Grams per Liter.—Once more the effect of sweeping is greater and the pressure upon the float rises to 3.40. However, the solution recovers within thirty minutes. On the other hand, the outstanding observation is that upon compression the initial pressures are again greatly increased, being 7.08 for 92.5% compression. Nevertheless, the final characteristic pressure is 0.51–0.55 attained in about forty-five min.

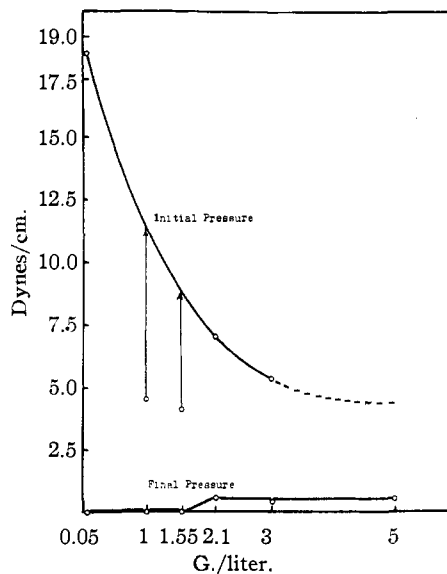


Fig. 9.—Laurylsulfonic acid, Procedure V, compressed 92½%.

1.55 Grams per Liter.—The effect of sweeping clean is relatively enormous, being now 18.02 dynes per cm., and requiring several thousand minutes for recovery. This is illustrated in Figs. 1 and 2.

The most important single observation is the fact that no final pressures are obtained upon compression, however great. Curiously, the time required for the initial pressure produced by compression to disappear rises with amount of compression until a sharp maximum is reached, after which it is very short. As an example, at 10% compression it required only six minutes to drop to zero, whereas at 87.5% compression it required 950 minutes, while at 96.5% compression it dropped to zero in only twelve minutes.

One Gram per Liter.—Now that the minimum surface tension has been passed, the great increases in time required to restore the surface after sweeping clean are no longer observed as in the foregoing series of higher concentrations, but drop again from a few thousand to a few

hundred minutes. However, the initial effect of sweeping is far greater, being 23.54 dynes.

Upon compression there is again no permanent pellicle, but the initial pressures are still greater than with the 1.55 g. concentration. Once more the time for the initial pressure to disappear increases with compression but suddenly falls after 75 to 87.5%.

One-half Gram per Liter.—This very dilute solution still gives definite pressures. Sweeping produces only a slight pressure difference, which disappears in fifteen minutes. However, compression produces enormous initial pressures, up to 18 dynes per cm., much higher than those for the less dilute solutions but they disappear within a few seconds for 10% compression, three minutes for 75% compression and about thirty sec. for 92.5% compression.

Discussion

Considerations of space prohibit reproduction in full of the varied and numerous data⁶ (62 tables and 44 graphs). Instead, we can merely supplement the information already given by a series of summary tables and graphs showing how the results depend upon concentration for lauryl sulfonic acid solutions. These should be compared with those given by McBain and Perry for hydrocinnamic acid.

TABLE I

Concn., g./liter	Max. press. diff., dynes/cm.	Time interval, min.
5	0.51	15
3	1.34	(340) ^a
2.1	3.40	30
1.55	18.02	3000
1	23.54	450
0.05	0.40	15

^a Result uncertain owing to drift of the zero point.

TABLE II

Concn., g./liter	Initial pressure, dynes/cm.	Final pressure, dynes/cm.	Time interval
Procedure V. 10% Compression			
5	0	0	..
3	0.10	0	..
2.1	0.40	0.12	<30 min.
1.55	1.47	0	6
1	2.13	0	20
0.05	1.99	0	20 sec.
Procedure V. 50% Compression			
5	0.72	0.20	..
3	1.02	0.13	60 min.
2.1	3.36	0.33	60
1.55	2.84 ^a	0	400
1	4.15 ^a	0	50
0.05	11.09	0	3

(6) Stanford University theses are being made available in bibliofilm, U. S. Dept. of Agriculture.

Procedure V. 75% Compression

5	1.28	0.31	...
3	2.28	0.36	60 min.
2.1	4.60	0.54	40
1.55	3.10 ^b	0	360
1	4.45 ^b	0	1435
0.05	13.62	0	3

Procedure V. 87.5% Compression

5	2.56	0.52	17 min.
3	4.16	0.37	60
2.1	6.40	0.54	45
1.55	3.60 ^c	0	950
1	4.32 ^c	0	90
0.05	15.72	0	1

Procedure V. 92.5% Compression

5	...	0.52	...
3	5.30	0.36	115 min.
2.1	7.08	0.55	60
1.55	4.06 ^d	0	...
1	4.57 ^d	0	40
0.05	18.30	0	40 sec.

^a These concentrations were compressed from 10 to 50%, instead of from 0 to 50%.

^b These concentrations were compressed from 50 to 75%, instead of from 0 to 75%.

^c These concentrations were compressed from 75 to 87.5%, instead of from 0 to 87.5%.

^d These concentrations were compressed from 87.5 to 92.5%, instead of from 0 to 92.5%.

To sum up, it is evident that but little is known of the properties of the surface layers of solutions. The assumption current during the past twenty years that clean solutions may be regarded as uniform solution right up to a bounding monomolecular film is untenable; and the common interpretations of their hypothetical monomolecular film as gaseous, etc., become very doubtful. This is in complete contrast to the well-established and beautifully simple behavior of oil films on water or insoluble contaminations upon solutions.

Summary

The film balance when applied to ordinary solutions yields a complex series of novel results which bear but little relation to previous conceptions derived from analogy with insoluble monomolecular films floating on water; and thus a new field is open to investigation.

Particularly striking is the fact that the various phenomena of surface pressure and of time frequently pass through a high maximum in an intermediate range of dilute solution. Again, whether a pellicle forms or not depends both upon the concentration and the degree of compression

of the surface. Some substances apparently never form it. When it is formed and sufficiently compressed, the final pressure is characteristic only of the substance. On the other hand, the

initial pressure may be greatest where the final pressure vanishes.

STANFORD UNIVERSITY, CALIFORNIA

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Observations of Surface Tension in the PLAWM¹ Trough

BY J. W. MCBAIN, J. R. VINOGRAD² AND D. A. WILSON

In recent years attention has been drawn to the long time effects observed in the surface tensions of solutions. The time effects are of a much higher order of magnitude than can be accounted for by ordinary diffusion. Likewise great interest attaches to solutions whose surface tensions are of Type III. In these, a trace of solute lowers the surface tension to a fraction of that of the solvent, whereupon further addition leaves the surface tension constant or may cause it to pass through a minimum in very dilute solution. In either case, application of the Gibbs theorem, where the slope of surface tension against concentration is zero, would seem to predict zero adsorption, just where the surface tension is most greatly lowered and where adsorption is actually pronounced.³ About one hundred such cases have been reported.⁴

In attempting to verify the existence of these reported effects it is highly desirable to find a method of measuring surface tension which shall fulfil the requirements that (a) the surface is static and undisturbed, (b) that it is swept free from contamination, (c) that it is observed for an adequate period and (d) that evaporation is avoided. None of the previously existing methods fulfilled all of the first three requirements and every method had been criticized by other authors.⁵ For these reasons the PLAWM trough was devised. In this, the superficial floating barrier of the Pockels-Langmuir-Adam surface film trough is replaced by one which is water-tight and yet flexible. This was done by cementing to the bottom and walls of the trough with dicetyl a sheet of vulcanized dipped latex rubber 0.004"

(0.1 mm.) thick of density 1.02 especially made for us by the Miller Rubber Company, Inc., Akron, Ohio. This delicate rubber partition was also fastened to a float in the line of the surface. Thus, the trough is separated into two compartments, one of which may contain water, the other solution; both have plane surfaces which can be swept. If hydrostatic effects are equalized, the only force acting upon the float is the difference of surface tension on the two sides.

Although the PLAWM trough is simple in principle, it is very exacting in practice. However, it here serves its purpose of demonstrating beyond question the existence of Type III curves and it is of much interest to compare the results obtained by this method with those from a number of other current methods.

The Apparatus

As the basis, we used a trough made for us through the courtesy of Dr. N. K. Adam. It consisted of a brass tray $50 \times 14 \times 2$ cm. carrying a compound torsion balance. The tray was given 18 superimposed coats of Bakelite lacquer, each baked on at 150° . The same treatment was given to all other metal parts which might come in contact with liquid, with the exception of the float which consisted of a 12-cm. strip of platinum-iridium folded longitudinally. The rubber membrane was first attached with dicetyl to a U-shaped frame and then at the height of the meniscus to the float; the whole frame was then fitted water-tight into the trough with dicetyl. Two strands of 0.04 mm. silver wire connected the float to the torsion mechanism and mirror.

In the original experiments of Wilson, which are here referred to only briefly, the rubber membrane was made with folds so voluminous that it was found experimentally that the hydrostatic pressure on both sides was equalized within fifteen to forty-five minutes, after addition of more water or solution, as was shown by the float returning to the original zero point. In the present experiments only about 1 cm. extra of rubber was allowed on both sides and under the float, but the two compartments of the trough were connected by a siphon of 2 cm. bore which could be closed with stopcocks.

All the measurements were made in an atmosphere which was practically saturated with water vapor. The case

(1) Pockels-Langmuir-Adam-Wilson-McBain; see McBain, Ford and Wilson, *Kolloid Z.*, **78**, 1-9 (1937).

(2) Bristol-Myers Company Research Fellow.

(3) J. W. McBain and L. A. Wood, communicated to the Royal Society, 1939.

(4) For references, see J. W. McBain and G. F. Mills, Reports on Progress in Physics, Vol. 5, p. 30, 1939, published by the Physical Society, Cambridge University Press, England.

(5) See also for example Bartell, Culbertson and Miller, *J. Phys. Chem.*, **40**, 885 (1936).