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 PLAWM[1] Trough

By J. W. McBain, J. R. Vinograd[2] 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 × 14 × 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

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[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).

surrounding the trough had been made water-tight by coating with paraffin, and water was allowed to stand on the floor to a depth of a few centimeters. Streamers of cheesecloth dipped into this pool of water and extended to the top of the case. A hygrometer always read 100% relative humidity. Access to the instrument was made by means of small sliding doors.

Experimental Technique

To begin each run the trough was rinsed repeatedly with distilled water which was drawn out through the top of the siphon. Conductivity water from a Barnstead still was then added to both sides, and the surfaces were swept at least five times. Three Bakelited quartz sweeps were manipulated so that two were always in position near the immersed ends of the siphon but on the side toward the float. The stopcocks of the Pyrex siphon were not closed until the light beam of the optical indicator came to rest. After closing the stopcocks the surfaces were again swept and the light beam was observed over a time interval similar to one considered in the measurement. The experiment was begun only if the position of the optical indicator and thus that of the float did not change.

A sweep was placed within 3 mm. of the platinum-iridium float and a measured amount of solid was added to the water in the large compartment outside this sweep. In the case of the slowly soluble hydrocinnamic acid the solid was finely ground and then sprinkled on the surface through a platinum gauze. This considerably enhanced the rate of solution which otherwise for concentrated solutions might require days. The solution was then stirred until it was homogeneous, using a quartz rod cleaned by heating to redness. The experiment was begun by drawing the sweep over the large surface from the float position to a position near the end of the trough. The moment of sweeping was considered the beginning of the experiment.

For the period of observation the light beam and thus also the float were maintained at a fixed position by adjusting the torsion wire. The experiment was in some cases repeated by sweeping the solution surface a second time. The observation of each solution was continuous for some hours, with the object of ascertaining when the value became constant. At the conclusion of the surface tension readings, the solutions were analyzed, the hydrocinnamic acid by the Zeiss interferometric refractometer and the lauryl sulfonic acid by titration with potassium hydroxide.

Experimental Tests

In the actual experiments the siphon was kept closed after the initial equalization of hydrostatic pressure. However, preliminary observations were made as follows.

With the siphon open the displacement of the float due to the addition of 5 cc. of water is nullified in one minute.

With the siphon closed when 5 cc. of water was removed the original position of the light beam was reëstablished when the water was replaced in the trough.

The float returned to the original position after stirring as soon as the violent disturbance died down.

The addition of water to one side gave a definite effect proportional to the amount of water added, 1.02 dynes/cm./g. of water. An increment of 0.60 dyne/cm./g. was observed when varying amounts of sucrose up to 10 g. were added. The effect of the maximum amount of sucrose used on the surface tension of water is 0.05 dyne/cm. and this was below the sensitivity of the apparatus. While the addition of pure water influences the float only through the effect of increased depth upon hydrostatic pressure, the addition of soluble solids influences it partly through the change produced in depth but also through the change in density of the solution and these effects may reinforce or partly neutralize each other depending upon the actual volume effects for the particular case. The results obtained were corrected for this hydrostatic effect.

The apparatus was calibrated frequently by hanging weights on the lever arm of the torsion balance. With the 0.18 mm. phosphor-bronze torsion wire used in experiments on hydrocinnamic acid the conversion factor was 0.136 dyne/cm. per degree torsion. In view of the large surface tension lowering of lauryl sulfonic acid, 0.25 mm. phosphor-bronze wire was used. The corresponding factor was 0.648 dyne/cm. per degree torsion. Since torsions could be read to 0.1 degree the uncertainty in the readings for lauryl sulfonic acid solutions corresponds to 0.25 dyne/cm.

Materials

The potassium laurate was a special preparation made by Kahlbaum mentioned in previous communications. The hydrocinnamic acid was made by Eastman Kodak Co. and was purified in the usual manner by cooling an aqueous solution saturated under 50° (18 g./liter) toward room temperature, rejecting the crystals separating but taking those formed on further cooling to 0°. Sodium butylbenzene sulfonate was prepared by the method of Neville and Jeanson.[6] The lauryl sulfonic acid was a specially pure specimen prepared by M. E. Synerholm under the direction of Dr. C. R. Noller.

Preliminary Results

In the experiments of Wilson in 1936 a Lloyd and Scarth ring tensiometer was also incorporated in the PLAWM trough. The surface tensions so measured were in agreement with those yielded by the PLAWM trough.

Of much interest was the observation that whereas soap solutions commonly exhibit a pronounced minimum in their surface tension curves,[7] and the potassium laurate behaved likewise, addition of 0.0116 *N* potassium hydroxide, added with the intention of suppressing hydrolysis, eliminated this sharp minimum occurring at about 1 g./liter by causing all the higher concentrations to remain at this low value.

The results with sodium butylbenzene sulfonate are given in Fig. 1, both trough and tensiometer exhibiting a minimum similar to that described by Neville and Jeanson.[6] Here the minimum occurs in much less dilution and it remains to be

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[6] Neville and Jeanson, *J. Phys. Chem.*, **37**, 1001 (1933).

[7] "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 449–450.

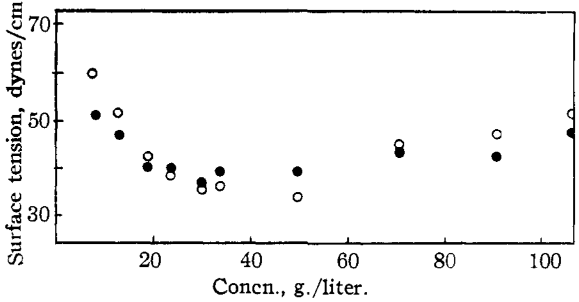

Fig. 1.—Graph showing minimum in surface tension of aqueous sodium butylbenzene sulfonate corroborating Neville and Jeanson[6]; ○, PLAWM; ●, ring method.

proved whether further purification (hydrolysis is of course impossible) might flatten out the minimum. However, Wood[3] found a very definite minimum in more dilute solution with moderately pure butylbenzene sulfonic acid.

Results with Solutions of Hydrocinnamic Acid

These solutions of β-phenylpropionic acid exhibit a surface tension which changes over long periods of time. Whereas until recently it has always been taken for granted that the surface tension of ordinary dilute solutions would change from the perfect dynamic or instantaneous value, almost equal to that of the solvent, down to the final or equilibrium value as fast as the concentration of the surface zones could be adjusted by classical processes of diffusion, a matter of a small fraction of a second, we here have another clear case like that of Adam and Shute[8] showing that the surface tension is not fully lowered until after enormously greater periods of time.

It is equally difficult to measure the perfect dynamic surface tension of a solution and its perfect final static or equilibrium surface tension. All existing measurements probably fall between the two. Drop number and drop weight and maximum bubble pressure upon which many investigators have relied prove to be semi-dynamic. The ring methods are better in that the surface may be aged for days before the ring is pulled through the surface, but this latter process is accompanied by stretching and formation of new surface.

We are fortunate in being able to present in Fig. 2 data obtained by Dr. Donald Purdie of Cambridge, England, with a Sugden maximum bubble pressure equipment, together with the data of Professor E. A. Hauser of Massachusetts Institute of Technology with his pendant drop method, the measurements of Drs. R. C. Swain and C. R. Bacon with the drop weight method, those of Dr. G. F. Mills with the ring method of Harkins and Jordan, together with our own results using the PLAWM trough. It is abundantly clear that the surface tension of any one solution is a function of time over long periods and that no method of measuring surface tension measures either the true initial or the true final value.

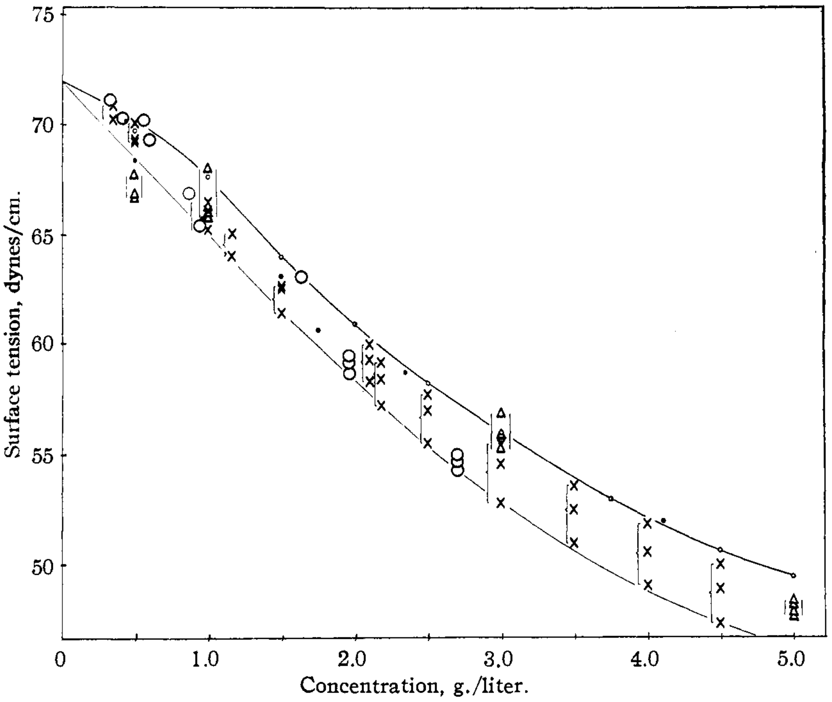

Fig. 2.—Graph showing effects of time upon surface tension of aqueous hydrocinnamic acid as studied by many methods: ×, ring method, uppermost point at age of surface 5 min., next point below at 1 hr., lowest point 9 hrs.; ○, drop weight at 30 sec.; ●, maximum bubble pressure for releasing bubbles; Δ, pendant drop method, uppermost at 15 sec., followed in order by 60, 120 and 300 sec.; ◯, PLAWM trough, for 2 and 2.7 g./liter at 15 min., 60 min. and 120 min. in order, but for the more dilute solutions only one determination between 30 to 60 min.

With the sessile bubble, etc., the surface is small in comparison with the bulk of the solution

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(8) Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

and impurities may concentrate therein without possibility of sweeping. With the PLAWM trough there is a large area (560 sq. cm.) whose surface tension is found to be but little affected by stirring or by disturbing a small portion of it. It may be swept an indefinite number of times to eliminate surface contamination. These latter points may and should be adopted in the ring method, which then would become with the precautions indicated by Mills perhaps the most informative and trustworthy method of measuring surface tension.

In Fig. 2 we have drawn the uppermost curve through the data for drop weight obtained with drops thirty seconds old. The bottom curve is that for the surface tensions by the ring method at the ostensible age of nine hours. Between these two arbitrary curves all the other data are bracketed. The methods that are capable of showing change with time show it. In plotting the data, all measurements were arbitrarily corrected to 25° by adding the difference in surface tension of pure water at 25° and the temperature of measurement. Only the pendant drop and the PLAWM trough were used at 25°. The drop weight and the ring were at 22–23°, and the bubble pressure at 21.5°, so that the data may be easily reconverted.

Results with Lauryl Sulfonic Acid.—Again we are fortunate in being able to present Fig. 3 which critically establishes the existence of Type III curves of surface tension with a minimum in extremely dilute solution. The data given are those of Dr. H. B. Bull of Northwestern Medical School using the Wilhelmy method, those of Dr. L. A. Wood with the ring method (using swept carefully protected surfaces), after periods up to forty-eight hours, those for the PLAWM trough, and two measurements for extremely dilute solutions by Professor Grinnell Jones and Dr. W. A. Ray of Harvard with their precision capillary method which gave for 0.0285 and 0.2225 g./liter, respectively, 0.9936 and 0.9141 times that of water for 25°.

Once more the surface tension is a function of time over very long periods, but for the present purpose we are only interested in the proof that the equilibrium surface tension curve is of this form.

Differential Results with Lauryl Sulfonic Acid.—Since it has been shown that observed surface tensions of solutions are somewhat arbitrary values dependent upon time and the method of measurement, a new approach was made to establish that in the very dilute solutions containing between 1.5 and 2 g./liter the surface tension does actually increase with concentration. For this purpose the surface tension in the PLAWM trough was first measured for a solution containing about 1.55 g./liter and the establishment and reëstablishment of a surface tension of 30 dynes/cm. eighty minutes after each sweeping was observed. As is shown in Fig. 4 the surface tension fell 7 dynes between the first and eightieth minutes.

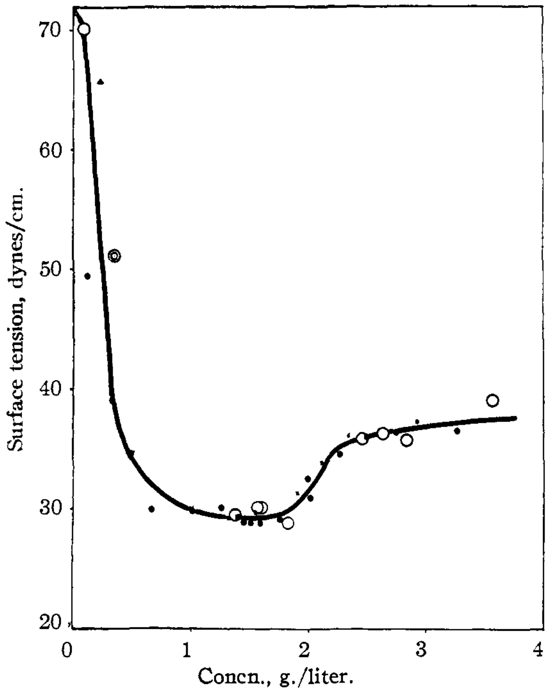

Fig. 3.—Surface tension of lauryl sulfonic acid exhibiting Type III curve with minimum at 1.55 g./liter. The values shown represent the final lowering of surface tension at the times stated: ○, PLAWM trough at 60 min.; ◎, PLAWM trough at 10 hrs.; ×, Wilhelmy method at at least 45 min.; ●, ring method at 1 to 2 days; △, capillary rise method, time not stated.

Thereupon, additional lauryl sulfonic acid was put in to bring the concentration to about 2.5 g./liter. Figure 4 shows that now the surface tension was 36 dynes/cm., almost independent of age or sweeping. This differential method which upon repetition yielded the same results proves critically the existence of the minimum in the surface tension curve which has led to the unsolved contradiction between the thoroughly established[8] actual positive adsorption and the zero and negative adsorptions apparently demanded by the Gibbs theorem.

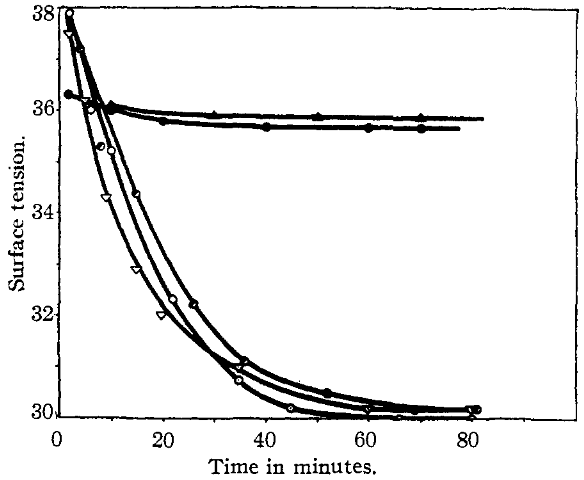

Fig. 4.—Differential method with PLAWM trough to establish existence of minimum in surface tension of aqueous lauryl sulfonic acid: ○, ∇, ◐, surface tension observed after first, second and third sweepings, respectively, for 1.575 g./liter, showing surface tension falling from 38 to 30 dynes/cm. in 80 min.; thereupon for 2.460 g./liter showing surface tension raised to and remaining at 36 dynes for 80 min., and also up to 260 min., ●, for first sweeping; ▲, after second sweeping.

Tartar and Cadle reported at the Sixteenth National Colloid Symposium, 1939, even more striking minima in their surface tension curves for the sodium straight chain alkyl sulfonates. Likewise, Adam and Shute[9] find definite minima for aqueous cetyltrimethylammonium bromide at 0.045% and for sodium dodecyl sulfate at 0.01 *N*; their time effects are similar to ours. It is of interest to note that, owing to the long time required for dilute solutions of lauryl sulfonic acid to exhibit full lowering of surface tension as compared with the almost immediate attainment of it in solutions containing over 2.5 g./liter, Wood found for very short times a Type I curve rapidly sagging down into the position shown by our Type III curve in Fig. 3. Naturally the thermodynamic theorem of Gibbs refers only to the final equilibrium value and not to any arbitrary value between that and the initial instantaneous dynamic surface tension.

Other Uses of the PLAWM Trough.—Since it has been abundantly shown[9] that the ordinary film balance strikingly fails to measure surface tension of solutions and that complicated time effects reach their maximum in an intermediate range of dilute solution, it becomes of great interest to carry out similar experiments with the PLAWM trough which of necessity measures the actual surface tension and the influence thereon of such procedures as sweeping and compression. Indeed, this will be necessary in order to interpret the results obtained with the film balance. However, the latter is sufficient to show that the effect of sweeping the surface of a solution of lauryl sulfonic acid, while negligible in infinite dilution and again at solutions containing 2.5 g./liter, is so great in a solution containing 1.5 g./liter that an error of over 2 dynes remains if the surface tension is measured as soon as one hour after sweeping.

Summary

The PLAWM trough, consisting of a film balance divided into two compartments by a water-tight flexible float, has been applied to solutions of hydrocinnamic acid, potassium laurate, sodium butylbenzene sulfonate and lauryl sulfonic acid.

In conformity with data by other recognized methods kindly supplied us by other workers, it has been shown that the surface tension of solutions of hydrocinnamic acid is not fully established until after periods of time enormously greater than those expected from classical diffusion processes.

The existence of Type III curves with a minimum has been critically established. In these a trace of solute reduces the surface tension of the solvent to a fraction of its value, whereupon further small addition raises the surface tension again to a still low maximum or constant value. This has been shown for lauryl sulfonic acid (and also for sodium butylbenzene sulfonate), again in conformity with data kindly supplied us by other workers. With potassium laurate addition of alkali appears to lower the flat maximum to the value of the minimum.

It is pointed out that the PLAWM trough will be invaluable in repeating and interpreting the surprising results obtained with clean solutions of soluble substances with the Pockels–Langmuir–Adam film balance.

Stanford University, Calif.

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(9) McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939); McBain and Spencer, This Journal, **62**, 239 (1940); also references to Doss quoted therein.