[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

The Effect of Dissolved Salts on Insoluble Monolayers

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Part I. Monolayers on Water

This paper is a summary of our work during the last three years in which we have studied the properties of monolayers of stearic acid and some other substances on water containing low concentrations of metallic salts at various values of *p*H. The properties are sometimes so sensitive to the presence of dissolved salts that concentrations as low as 10^{-8} molar may be detected (3×10^{-10} g. of aluminum per cc.).

Many of the methods we have used are applicable in general to the study of insoluble nonvolatile films on water; that is, to those that can withstand pressure exerted by barriers without loss of material from the film. We shall give a few examples of such applications.

In some studies of monolayers of stearic acid adsorbed at the interface between petrolatum and water[1] it had been found that very low concentrations of calcium ions (less than that which corresponds to the solubility of calcium carbonate in 0.02 *N* sodium carbonate) cause the area per molecule in the monolayer to decrease from 90 to 20 sq. Å. and make the film rigid.

Dr. Blodgett's studies of the building up of multilayers[2] showed that concentrations as low as 3×10^{-6} molar of calcium carbonate permitted the formation of these multilayers on alkaline water. Later work[3] showed that traces of substances present in distilled water from several sources, all of which had specific resistances of the order of 10^6 ohms cm. (without removal of carbon dioxide), were found to have appreciable effects on multilayers of barium stearate and upon the conditions under which they could be built. Copper, zinc and lead salts purposely added, at concentrations of 10^{-6} *M*, also had profound effects.

A few years ago[1] methods were developed for determining the equation of state (*F–a* curves) for adsorbed films of stearic acid at the interface between hydrocarbons, liquids and water. Complete data were given for these interfacial films between petrolatum and 0.01 *N* hydrochloric acid solution and a few data were given for films on 0.01 *N* sodium hydroxide.

Later, because of their biological interest, we attempted[4] to obtain *F–a* curves for a series of different values of *p*H from 2 to 10 and to study the effect of additions of potassium, sodium, calcium and magnesium chlorides. We wished to apply Gibbs' equation to determine the amount of OH^- ion adsorbed and to check the accuracy of the data. However, we ran into serious difficulties which originated from minute and uncontrollable traces of impurities in the distilled water and in the added salts. We decided, therefore, before continuing this work to make a detailed study of the effects of salts upon stearic acid monolayers at an air–water interface where similar effects may be expected.

We have chosen stearic acid for most of these studies because of its known reactivity with metallic ions to form insoluble compounds. Thus polyvalent cations should be very strongly adsorbed upon the carboxyl groups which lie at the under side of the stearic acid monolayer on water. Cetyl alcohol and cholesterol monolayers are comparatively little affected in their properties by *p*H and by dissolved salts.

The properties of the stearic acid monolayers were found to be so greatly modified by such small traces of certain salts that it seemed unwise to make accurate measurements of these properties. We have preferred to study properties which can be observed quickly by simple means. We hope soon to make quantitative studies, now that the precautions for obtaining reproducible conditions are definitely known.[5]

Theory of the Adsorption of Salts by Monolayers

The modification of a stearic acid monolayer by the presence of salts in the substrate is usually due to adsorption of the salt on the under surface of the monolayer, but in some cases[6] "penetration" occurs; that is, adsorbed atoms or molecules take positions between the molecules of the original monolayer.

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(1) I. Langmuir, *J. Franklin Inst.*, **218**, 143–171 (1934).

(2) K. B. Blodgett, THIS JOURNAL, **57**, 1007 (1935).

(3) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(4) I. Langmuir, *Science*, **84**, 379 (1936).

(5) Three short papers [R. J. Meyers and W. D. Harkins, *Nature*, **139**, 368, (1937); J. S. Mitchell, E. K. Rideal and J. H. Schulman, *ibid.*, **139**, 625 (1937); C. Robinson, *ibid.*, **139**, 626 (1937)] have appeared recently on the effects of traces of metallic ions on air–water molecules.

(6) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.* (London), **B122**, 29–57 (1937).

The relation between the composition of the solution and that of the monolayer may be represented by an equation which is called the adsorption isotherm. In general, there will be one such equation for each adsorbable component.

In some very simple cases of adsorption where there is only one adsorbed component the adsorption isotherm is of the hyperbolic type given by

$$\Theta/(1 - \Theta) = Ap \qquad (1)$$

where Θ is the fraction of the number of surface cells (elementary spaces) occupied by the adsorbed substance, p is osmotic pressure (strictly the fugacity) in the solution and A is a constant at a given temperature. This equation should hold rigorously only if (1) each cell can hold only one molecule, and (2) the molecules in separate cells exert no forces on one another.

It can hardly be expected that this simple equation will hold in the cases we shall have to consider. The highly polar molecules of metallic stearates in adjacent cells almost certainly exert strong forces on one another. Furthermore, each adsorbed barium atom presumably can combine with two stearic acid molecules.

A theory previously proposed[7] showed that in some cases in which each adsorbed molecule dissociates upon adsorption and so occupies more than one cell, the adsorption isotherm should be given by

$$\Theta/(1 - \Theta) = Ap^n \qquad (2)$$

where n is $^1/_2$ (or $^1/_3$) if two (or if three) cells are occupied.

One of us (L.) recently has worked out a theory of adsorption (unpublished) where each molecule without dissociation prevents adsorption in several adjacent cells because of its large size. This has led to a complicated expression for the adsorption isotherm which over a wide range is well represented by the equation

$$\Theta/(1 - \Theta)^n = Ap \qquad (3)$$

where $n = 2.5$ or sometimes even higher values.

If we knew the equation of state of the monolayer, *i. e.*, the complete *F–a* curve and its dependence upon the presence of metallic constituents, we could theoretically obtain the adsorption isotherm by an integration of Gibbs' equation. However, if more than one component must be considered, Gibbs' equation gives a set of partial differential equations whose solution is very difficult and which involves not only integration constants but arbitrary functions. So an approach from this direction seems hopeless at present.

Without more detailed knowledge of the forces between adsorbed molecules than we now possess we therefore cannot derive an exact adsorption isotherm. It is best therefore to adopt a flexible empirical equation which will incorporate the following features: (1) It should reduce to Eqs. (1) and (2) in special cases. (2) It should possess characteristics suggested by the law of mass action. (3) It should show that as the concentration of any component in solution is raised indefinitely the content of that component in the adsorbed layer slowly approaches a limiting value (saturation).

The following empirical equation for a single component system satisfies these requirements

$$\Theta/(1 - \Theta)^n = Ap^m \qquad (4)$$

where n, m, and A are empirical constants. For cases of several components whose covering fractions are Θ_1, Θ_2, etc., the equation may be generalized into

$$\begin{aligned} \Theta_1/(1 - \Theta_1 - \Theta_2 \ldots)^{n_1} &= A_1 p^{m_1} \\ \Theta_2/(1 - \Theta_1 - \Theta_2 \ldots)^{n_2} &= A_2 p^{m_2}, \text{ etc.} \end{aligned} \qquad (5)$$

If we take a metallic element M which can react with stearic acid H*St* to form an insoluble stearate MSt_ν, the reaction between the ions of the substance and the stearic acid is

$$M^+ + \nu HSt + \nu OH^- = MSt_\nu + \nu H_2O$$

where ν is the valence of the cation. Thus, according to the law of mass action, the presence of the hydroxyl ion is at least as important as the presence of the metallic ion.

For the present, let us make the simplifying assumption $n_1 = n_2 = 1$. For the case of the adsorption of barium salts p should be proportional to the activity of barium hydroxide so that Eq. (5) becomes

$$\Theta/(1 - \Theta) = A([Ba^{++}][OH]^2)^m \qquad (6)$$

Empirically for the adsorption of barium by stearic acid monolayers from a 10^{-4} *M* solution of barium carbonate we found[8]

$$\log_{10}\{\Theta/(1 - \Theta)\} = -2.41 + 0.367\,(pH) \qquad (7)$$

The relation between pH and (OH$^-$) is given by

$$\log_{10}(OH^-) = (pH) - 14 \qquad (8)$$

Taking the logarithm of Eq. (6) and combining with Eq. (8) the equation takes the same form as Eq. (7) if the barium concentration is constant. This comparison gives $m = 0.184$ and enables us

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[7] I. Langmuir, THIS JOURNAL, **40**, 1373 (1918).

[8] I. Langmuir and V. J. Schaefer, *ibid.*, **58**, 284 (1936).

to take into account a change in barium concentration

$$\log_{10} \{\Theta/(1 - \Theta)\} = -1.68 + 0.184 \log_{10} [\mathrm{Ba}^{++}] + 0.367\,(p\mathrm{H}) \quad (9)$$

For a barium solution at 10^{-4} M this agrees with Eq. (7).

Where we have two kinds of cations, one of them being a monovalent cation M_1^+, and the other a divalent ion M_2^{++}, we should then be able to write two equations

$$\begin{aligned} \log \{\Theta_1/(1 - \Theta_1 - \Theta_2)\} &= C_1 + m_1 \log [\mathrm{M}_1^+] + m_1\,(p\mathrm{H}) \quad (10) \\ \log \{\Theta_2/(1 - \Theta_1 - \Theta_2)\} &= C_2 + m_2 \log [\mathrm{M}_2^{++}] + 2m_2\,(p\mathrm{H}) \end{aligned}$$

where C_1, C_2, m_1 and m_2 are constants characteristic of the cations. Thus ferric ions are strongly adsorbed by stearic acid monolayers at pH 2, and aluminum ions at pH 3 to 5, whereas barium is strongly adsorbed only at $p\mathrm{H} > 6$ and sodium at $p\mathrm{H} > 8$. These equations afford a simple explanation of the antagonistic action between certain ions. For example, it is known that if the calcium content in sea water and the potassium content are increased in the same ratio, marine organisms suffer much less disturbance than if the concentration of either ion alone is changed. A series of experiments which C. N. Moore and one of us have carried out with the effect of salts on adsorbed films of stearic acid at the interface between oil and water[4] has shown clear evidence of this antagonistic action. If, at pH 7, the calcium content is increased until the interface becomes perceptibly solid, it becomes liquid if we add sodium chloride, and more calcium has to be added to make the film rigid again.

The relative amounts of adsorption of different ions depend mainly on the values of C_1 and C_2 in Eqs. (10). Let us assume then that C_2 is much greater than C_1. Then if we have equal concentrations of two elements, M_2 will be much more strongly adsorbed than M_1, and at high pH the surface is practically saturated with M_2. However, by adding a sufficient concentration of M_1 the M_2 adsorbed on the surface can be replaced by M_1. In rough experiments both with stearic acid films at the interface between water and oil and with stearic acid monolayers on the water surface we have found $m_2 = 0.20 \pm 0.02$ for both copper and barium, and the coefficient of the (pH) term for these elements is about $2m_2$.

Apparatus Used in Experiments

The experiments which will be described in this paper can, for the most part, be carried out with the very simplest of apparatus involving the use only of one or two troughs, some barriers, chromium-plated slides on which to build up films and a Polaroid screen with which to observe the interference colors given by the built-up films.

1. **Troughs.**—For the studies of the properties of monolayers on water we usually use a trough 30 cm. long, 10 cm. wide and 1 cm. deep. For producing built-up films having many layers we employ a trough about 120 cm. long, 40 cm. wide, and 1 cm. deep, containing a well at the head end of the trough 9 cm. deep.

Several years ago we used troughs of brass but found troublesome effects due to contamination of the water by copper and zinc ions. Later we coated the troughs with paraffin. More recent work has shown that this does not wholly avoid contamination due to copper and zinc. In some cases, we have used a brass trough but to avoid contamination have placed molten paraffin in the bottom, set strips of chromium plated brass or glass (a little wider than the depth of the trough) against the side walls and then have covered the bottom of the trough and well with sheets of glass made to fit against the strips that form the edges. Aluminum either for troughs or barriers is liable to be extremely troublesome, for the most minute traces of aluminum have great effects upon stearic acid films.

We have obtained good results with brass troughs covered with several coats of bakelite which are baked on. The bakelite is then scraped off the edges that support the barriers.

A very satisfactory type of trough and one which is constructed easily is made from plate glass about 1 cm. thick. A single rectangular piece is used to serve as the base of the trough, and four strips 1 cm. or more wide are fitted (flat side down) to form the outer walls of the trough. Only one side of each strip need be straight. These strips are cemented into position by means of paraffin and all excess paraffin is scraped away from the inside of the tray. We find it advantageous to bevel off the outer edge of the glass strips so as to leave a bearing surface for the barriers not more than 3 mm. wide.

We have also used a trough heavily electroplated with 24-carat gold. This did not prove to be wholly satisfactory, for in the course of a few weeks traces of pitting began to appear. After water had stood in this trough for fifteen minutes some of the characteristics of the stearic acid monolayer (crumple pattern) became altered in a manner different from that which was observed with any other element except silver. The addition of a minute amount of gold chloride to the water produced a similar effect. It thus appears that enough gold dissolves in water in fifteen minutes to modify the properties of monolayers.

We have had this trough replated with gold and electroplated with two layers of rhodium. This plating is not satisfactory. If a stearic acid monolayer is spread on water from a quartz still in this trough, the surface viscosity at pH 5.8 of the monolayer at $F = 15$ dynes/cm. increases 10-fold within ten minutes and 1000-fold in thirty minutes.

We have also had good results from a nickel-plated brass trough which was subsequently plated with chromium. Such troughs, however, should not be used at low values of pH.

McBain, Adam and others have reported slow changes in monolayers when they remained for a long time on water in a trough and have recommended waiting for the completion of these changes before taking measurements. Our experience has been that such changes are indications of contamination of the water by materials from the trough. If a trough shows no evidence of such progressive changes during the course of experiments it may be presumed that contamination is not a disturbing factor.

It is frequently useful to distinguish between the two ends of a trough. We select one end, which we call the "head" of the trough, for most of the studies of the properties of monolayers. The opposite end we shall call the "piston end," for a movable barrier or "piston oil" is used there to exert a definite pressure upon the monolayer.

2. **Barriers.**—As barriers we prefer rectangular pieces of brass which are chromium plated. For use in acid solutions glass is more satisfactory.

Our experience in the use of paraffin as a substance with which to coat the barriers and the edges of the trough in order to make them non-wettable has been somewhat unsatisfactory. All samples of paraffin, even when heated with fuller's earth, give off traces of contamination on the water surface, such as can be detected by progressive changes in the contact angle shown by a drop of Petrolatum placed on the water. In place of paraffin we use ferric stearate which has a melting point about 98°.[9] This is applied to the edges of the trough which are heated above the melting point of the stearate. Then as the stearate begins to solidify it should be rubbed vigorously with a clean towel until nearly cold. This rubbing removes all but one monolayer which is very difficult to remove without an abrasive. This monolayer is both hydrophobic and oleophobic.[10] A surface prepared in this way always can be cleaned by merely rubbing it with a cloth even when it has been contaminated by oleic acid. It sheds no appreciable amount of impurity upon the surface of the water.

3. **Floating Barriers.**—To render visible the motion of a monolayer or to separate two monolayers which are at the same pressure we place on the surface of the water a floating barrier. In many cases this may be merely a narrow strip of paper having a length nearly equal to the width of the trough. Thus before spreading benzene upon the water we place such a barrier on the water surface about 2.5 cm. from the head of the trough and then apply the benzene drops between the barrier and the head end. The spreading monolayer pushes the paper strip along the trough, so that one can see how many drops are needed to cover the whole surface.

In other cases we use a silk thread as a floating barrier. This thread is waxed by soaking in a hot benzene solution of ferric stearate to make it non-wettable by water. The two ends are tied to glass hairpins which are fastened to opposite points on the sides of the trough near the middle. The thread is placed toward the head and the drops of the benzene solution are applied between the thread and the head of the trough.

A floating barrier consisting of a circular disk of paper (made waterproof by a dilute benzene solution of ferric stearate) of a diameter only a few mm. less than the width of the trough is particularly useful for measuring accurately the area of a liquid monolayer that is consumed in building up multilayers.

With monolayers which are elastic solids, such as those of protein, it is advisable to use a floating barrier in the form of an equilateral triangle with an apex pointing toward the head of the trough, the side of the triangle being nearly equal to the width of the trough. This design tends to force the protein monolayer against the sides of the trough and prevents leakage of piston oil past the barrier.

When a monolayer is to be kept for any great length of time on the surface of the water it should be covered by a plate of glass a few mm. above the water surface to protect it from dust. This glass plate extends to within about 5 cm. of the head end of the trough. If the monolayer is under pressure a fresh surface can always be brought out from under the glass by dipping a plate a few times at the head of the trough into the water.

4. **Indicator Oil.**—Instead of using talc, sulfur or floating barriers of paper to render visible the boundaries of a monolayer, we find it convenient to use an "indicator oil."[11] This is a duplex film of a hydrocarbon oil (with underlying adsorbed monolayer) of a thickness comparable with a wave length of light, so that it shows interference colors. Most spreadable substances (such as stearic acid) dissolved in Petrolatum give duplex films which are only metastable and soon break up into fine droplets. The hydrophilic substance which makes the most stable duplex films we have found is that obtained by the oxidation of petroleum oils such as those used in automobiles. We make up our indicator oil as follows.

Some petroleum lubricating oil is heated on a hot-plate for a few hours to a temperature at which it smokes. A sufficient amount of this oxidized oil is added to pure petrolatum to make the mixture spread out to a thin film which shows a first-order interference color (say an orange-yellow) when a small drop is placed on a clean water surface.

The color of this duplex film can be made to pass through the whole series of interference colors by subjecting it to increasing pressures F. A calibration of these colors against F, by means of a surface balance, thus gives a convenient method of applying any given small pressure F, up to about 10 dynes/cm.

Indicator oil may be applied as a minute drop from the end of a platinum wire to detect leakage of piston oil past a floating barrier.

We shall have occasion to describe other applications of indicator oil in our discussion of the properties of monolayers.

5. **Piston Oil.**—In studying the properties of monolayers on water or in depositing them upon solid plates it is important to subject them to a definite surface pressure F.

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[9] Ferric stearate is easily made by adding a slight excess of ferric chloride solution to a moderately strong aqueous solution of sodium stearate heated to about 70°. The heavy precipitate is filtered off into a cheesecloth bag and the water is wrung out of it. After washing a few times with distilled water it is dried, melted, and cast into sticks.

[10] We shall use the terms oleophobic and oleophilic to express general behavior of a surface toward oil-like substances such as petrolatum, hexadecane, etc.

[11] K. B. Blodgett, *J. Optical Soc. Am.*, **24**, 313 (1934).

Pressure can be exerted by a movement of a barrier at the piston end of the trough and the pressure measured by a surface balance. For many purposes the surface balance can be dispensed with by using a "piston oil," that is, an oil which serves the function of a two-dimensional piston by which a constant pressure can be applied. The oleic acid used as a piston oil was purified by being warmed with fuller's earth and centrifuged, and gave a pressure of 29.5 dynes/cm. at 25°. Triolein gave about 15 dynes and castor oil about the same. However, different samples of castor oil gave somewhat different values. We found that tricresyl phosphate gave 9 dynes. When it was desired to apply low surface pressures, the use of a calibrated indicator oil was very convenient. Thus an oil which we have been using gave a first-order yellow-red at $F = 0$, first-order blue at $F = 1.4$, second-order yellow at $F = 4$, second-order blue at $F = 5.2$, and third-order red at $F = 7.0$.

Since a piston oil, which consists of a pure substance, maintains a constant pressure on the monolayer of stearate during the building-up of multilayers of stearate on a plate it is more convenient to use piston oil than a surface balance with a movable barrier which would have to be continually adjusted after each monolayer is deposited. However, in order to be able to maintain constant pressures having any desired value and to avoid difficulties that sometimes arise from leakage of piston oil past floating barriers we have recently constructed a trough having a motor-driven barrier at one end and a surface balance at the other. An electric contact is operated by the surface balance, so that when the pressure rises above the predetermined value the motion of the barrier stops.

6. **Surface Balances.**—Most of the studies of monolayers and multilayers in this paper have been made without the need of a surface balance. The few measurements of *F-a* curves that we have taken have been made with a simple balance of the type described in a former paper[7] modified by using sapphire bearings from a standard watt-hour meter instead of knife edges, and a chainometric device to regulate the applied force. Leakage of the monofilm past the ends of the movable barrier was prevented by a thin rubber membrane stiffened in a vertical direction by linear reinforcements. This membrane was made by applying latex to a metal plate having fine parallel grooves cut in it; and it was then vulcanized. A simple and effective arrangement for pressures up to 10 dynes cm.$^{-1}$ is to allow the movable barrier of the surface balance to pass against a silk thread attached, with a little slack, to opposite sides of the trough.

A surface balance having quite sufficient accuracy for most purposes can be constructed in a few hours from fine drawn-out glass tubing, sealing wax and materials obtainable at a 5-and-10 cent store.

7. **Stirring Rod for Trough.**—In many of our experiments we have used such low concentrations of salts ($< 10^{-6}$ *M*) that the amount of solute needed to form a single layer of adatoms on the surface monolayer is a large fraction of that contained in the whole solution. Thus the film can become saturated only after the adsorbable ions have diffused through relatively large distances—a very slow process with diffusion coefficients of the order of 10^{-6} cm.^{2} sec.$^{-1}$ such as those in aqueous solutions.

Another factor that increases the difficulty is that convection currents in a liquid are greatly reduced by the presence of a monolayer on the surface.

We have been able greatly to accelerate the arrival of adsorbable substances at the surface by stirring the solution under the monolayer. For this purpose, in a trough 1 cm. deep, we use a quartz rod, 8 mm. in diameter which extends lengthwise through the trough 1 mm. below the water surface. The ends of the rod are bent at two right angles so that they extend out of the water and are supported on two rails at the ends of the trough. The monolayer is confined to the central part of the trough by barriers. Thus by sweeping the rod slowly across the trough, twenty times per minute, all the liquid is brought repeatedly into close proximity with the surface without disrupting the monolayer.

8. **Plates for Deposition of Multilayers.**—The thickness of monolayers and many other of their properties may be determined by depositing them on plates covered with multilayers having a total optical thickness of a little less than a quarter wave length of light of some chosen color.[3,12,13] For most purposes we have used plates of highly polished chromium-plated bars 1″ × 3″ (2.5 × 7.5 cm.) in size. For the deposition of 100 layers or less it is entirely satisfactory to raise and lower the plate through the monolayer by hand, but for building several hundred layers a simple manually operated device already described[2] is more satisfactory. We have tried several motor-driven devices of this sort, but have found no advantage over manual operation.

With the small trough, 10 × 30 cm., we often use strips of chromium-plated metal[14] about 1 cm. wide and 4 cm. long. By hand operation it takes only about forty seconds to build up 50 layers of barium stearate covering an area 1 × 1 cm.

For accurate measurement of the thickness of single monolayers within 1.5 Å. it is important that the underlying chromium surface be very uniform in optical properties. Thus an invisible film of oxide or other adsorbed film on the surface must not vary more than 1 Å. in thickness over the surface if measurements of the thickness of single monolayers are to be made with this accuracy.

To obtain a plate which is uniform within 1 or 2 Å. the chromium surface should be polished with rouge and then cleaned by rubbing on a flat surface covered with a wet cloth to which a high grade metallographic polishing powder such as Shamva has been added. This mild abrasive must then be removed carefully by swabbing the plate with cotton under water in a dish from which a constant stream of water is allowed to overflow. It is then dipped while still wet into water in a trough covered by a monolayer such as stearic acid under pressure. When it is raised slowly out through this water surface a B-monolayer is deposited which we shall call the initial monolayer.

For work in which it is unnecessary to determine film thicknesses within about 8 Å., plates may be used which, after having been covered by multilayers, are merely

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(12) I. Langmuir, V. J. Schaefer and D. Wrinch, *Science*, **85**, 76 (1937).

(13) K. B. Blodgett, *J. Phys. Chem.*, **41**, 975 (1937).

(14) At 5-and-10 cent stores, plates for electric wall switches are obtainable which consist of chromium-plated steel having a nearly optically plane surface. Many satisfactory "plates" can be sawed out of each.

rubbed vigorously with a clean towel. This leaves on the surface one monolayer which is hydrophobic and oleophobic and is an admirable initial layer for the reception of multilayers. This initial layer, however, is not quite so uniform in thickness as that obtained by deposition after cleaning with Shamva. An initial layer consisting of a rubbed-down layer of ferric stearate is also satisfactory where the highest accuracy is not necessary.

A sensitive indication of the uniformity of an initial layer may be obtained by cooling the back of the plate with running water and breathing on the front side so as to form a fog-like deposit of minute water drops. Lack of uniformity is made apparent by this "breath figure."

When multilayers are deposited on a small plate, the monofilm on the water must flow in converging lines toward the plate. This is only possible when the film is sufficiently fluid. Monolayers which are elastic or even brittle solids can often be deposited if the plate is made to extend across the entire width of the trough and the monolayer is cut loose from the sides of the trough by passing a wire along these sides.

For accurate comparison of the area of a monolayer on water with that of the monolayer after deposition on a plate, it is desirable to deposit the monolayer on a cylinder 2 or 3 cm. in diameter with vertical axis. In this way a more uniform deposition on the front and back sides of the plates is obtained.

Apparatus for Measuring Contact Angles

After having constructed somewhat complex apparatus for measuring within 0.5° the contact angle between a plate and a drop of liquid placed on it, we have adopted the following very simple device which gives results sufficiently accurate for all ordinary purposes (about 1°). The mirror is removed from an ordinary focusing-type pocket flashlight so as to provide a point source of light. A piece of cardboard having a slit 5 mm. wide and 9 cm. long is attached to the side of the flashlight so that the line of the slit is perpendicular to the axis of the flashlight and lies in a plane which passes through the point source of light. A disk of wood 10 cm. in diameter and 2 cm. thick is cut in half and one of these halves, in a vertical plane, is mounted on a horizontal piece of wood which serves as a table to support the plate on which the drop of liquid is placed. The plate is adjusted so that the near edge of the drop lies in the axis of the wooden disk. The edge of the disk has graduations giving angles from 0° at the top to 90° in the plane of the table.

To measure a contact angle, it is then only necessary to hold the flashlight at the side of the head so that through the slit one can observe the drop on the plate with both eyes. At sufficiently small angles of incidence a star-like point of light is seen in the drop which is the reflection of the flashlight lamp from the top surface. By gradually increasing the angle it is found that there is a critical angle at which this star of light disappears. A pointer attached to the graduated scale is moved until it is in the line of sight from the eyes to the edge of the drop. The scale reading then gives the contact angle B of the drop against the plate.

The work of adhesion W_S (in ergs cm.$^{-2}$) between the liquid and the monolayer on the plate is

$$W_S = \gamma(1 + \cos B) \qquad (11)$$

where γ is the surface tension (dynes cm.$^{-1}$) of the liquid. When water is used care must be taken to determine whether the water surface is contaminated by a complete monolayer from the plate, which might lower γ. The presence of a monolayer can be detected by observing the spreading of a minute amount of indicator oil brought into contact with the drop.

The advancing and receding contact angles are measured by mounting the table with a semicircular disk upon a board that can be tilted through any desired angle. These are obtained from measurements of contact angles at the near and far edges of the drop when the tilt of the board is increased to the point where the drop moves gradually over the surface.

By replacing the plate by a trough of water covered by a monolayer, on which there is a floating drop of oil, we may measure the two angles A_1 and A_2 which these surfaces make with the horizontal plane at the line of contact between the free surfaces of the two liquids. Let B_3 be the algebraic difference of these angles; that is, B_3 is the angle between the normals to the two free surfaces at their line of contact. Then we have Eq. (30).[15]

$$\gamma_{12}^2 = \gamma_1^2 + \gamma_2^2 - 2\gamma_1\gamma_2 \cos B_3 \qquad (12)$$

where γ_1 is the surface tension of the water as modified by the monolayer; *i. e.*, $\gamma_1 = \gamma_W - F$, γ_W being the value for clean water; γ_2 is the surface tension of the free surface of the oil drop, and γ_{12} is the interfacial surface tension between the oil and the water (modified also by the adsorbed interfacial monolayer). The work of adhesion W_L between the oil and the water (covered by the monolayer) is[16]

$$W_L = \gamma_1 + \gamma_2 - \gamma_{12} \qquad (13)$$

By substituting the value of γ_{12} from Eq. (12) into Eq. (13) W_L can be calculated from experimental data giving B_3. The values of W_L and W_S determined by these methods for various liquids placed upon monolayers on water and on solids should give valuable information regarding the presence of polar groups in molecules of monolayers and the manner in which these are able to respond to the attractive forces exerted upon them by solid or liquid substrates.

Solutions Used as Substrates

Many of the properties of stearic acid mono-

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[15] I. Langmuir, *J. Chem. Phys.*, 1, 756–776 (1933).

[16] See ref. (1), Eq. (10) and discussion on p. 157.

layers are greatly affected by the *p*H of the solution. Because of the effect of salts of alkali metals in modifying the action of divalent cations, it is undesirable in most cases to use ordinary buffer solutions. In unbuffered alkaline solutions the absorption of carbon dioxide from the air may lower the *p*H of the surface of the solution so as to alter the properties of the monolayer even when tests of the *p*H of the solution show no change. With higher concentrations of salts of metals which form difficultly soluble carbonates the absorption of carbon dioxide in alkaline solutions may cause the precipitation of carbonate in or under the monolayer.

By enclosing the trough containing the solution in a box in which carbon dioxide is eliminated or controlled, both these disturbing effects can be avoided; but as the flexibility of the experimental arrangement is thereby greatly decreased, we have preferred to work in free air and to choose conditions which will avoid errors due to carbon dioxide.

For example, by using concentrations of calcium or barium salts less than $10^{-4}\,M$, we do not obtain precipitation of carbonates even at *p*H 9. Distilled water in equilibrium with air gives *p*H 5.8.

To obtain higher values of *p*H we use solutions of the following compositions which we have found to be stable for many hours (or even days) in contact with the atmosphere.

*p*H	Concn. of $KHCO_3$, *M*	
6.8	2×10^{-4}	
7.1	4×10^{-4}	
7.8	2×10^{-3}	
8.2	3×10^{-3}	
8.5		$1 \times 10^{-2} M$ K_2CO_3
9.0	3×10^{-3}	$10^{-4}\,M$ KOH + $10^{-3}\,M$ NH_4OH

For values higher than *p*H 9 we use ammonium hydroxide and chloride or simply potassium hydroxide. Slight adjustments are sometimes needed after the addition of salts, but in most cases the concentration of added salts was too small to have an appreciable effect on the *p*H. We have usually determined *p*H by La Motte indicators, sometimes with a glass electrode.

For *p*H < 5.5 we have used unbuffered solutions of hydrochloric acid.

Distilled Water

The impurities present in distilled water from ordinary sources are sufficient to modify the properties of stearic acid films if *p*H > 5.

As a source of water from which to redistil the water for our experiments we use the output of a large still (6 liters per hour) in which the Schenectady city water is boiled by contact with a steam-heated coil. Although the specific resistance of this water is over 10^6 ohm cm., the viscosity tests and skim tests which we shall describe show that this water contains copper in a concentration of about $2 \times 10^{-6}\,M$, probably derived from some tin lined copper tubing through which the output of the still passes.

This water is then redistilled from a Pyrex glass vessel into a quartz tube condenser and collected in a Pyrex glass container (or sometimes in a 1-liter quartz flask). The specific resistance is again about 10^6 ohm cm.

We have also made tests of water condensed in tubes of pure copper, silver and platinum.

Rate of Diffusion of Ions to the Monolayer

In most of our experiments we have used concentrations of salts of $10^{-5}\,M$ and in some cases have varied the concentration between 10^{-3} and $10^{-9}\,M$.

At the lowest concentrations the total amount of solute is insufficient to saturate the monolayer and even at much higher concentrations the diffusion of solute to the monolayer is a relatively slow process unless the solution under the monolayer is stirred.

Consider a solution on which a monolayer is spread at time $t = 0$ and assume that every solute molecule that diffuses to the monolayer is adsorbed upon it. After the time t the number of molecules per sq. cm., σ, which become adsorbed is given by

$$\sigma = 2n(Dt/\pi)^{1/2} \qquad (14)$$

where D is the diffusion coefficient and n is the original concentration of the solute (molecules per cc.). This equation is derived on the assumption that there are no convection currents in the liquid and that it is of infinite depth.

The diffusion coefficient D for most salts in water is of the order of 5×10^{-6} cm.^{2} sec.$^{-1}$. For large organic molecules an estimate of D may be made from the empirical equation of Thoverts[17]

$$D = 8 \times 10^{-7}/\eta M^{1/2} \qquad (15)$$

where η is the viscosity of water and M is the molecular weight (O = 16) of the solute. Or the theoretical equation of Einstein[18]

$$D = kT/3\pi\eta\delta \qquad (16)$$

may be used, where δ is the diameter of the molecule which is assumed to be spherical.

If we take $D = 5 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ and express the concentration (c) in moles per liter equation (14) becomes

$$\sigma = 1.5 \times 10^{18}\,ct^{1/2} \qquad (17)$$

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(17) Thoverts, *Ann. Phys.*, **2**, 369 (1914).

(18) A. Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

A condensed monolayer of stearic acid contains 5×10^{14} molecules cm.$^{-2}$. Let γ be the number of stearic acid molecules per adsorbed ion of solute in a saturated film (about 12 for aluminum). Then Θ the fractional degree of saturation of the film is

$$\Theta = 3 \times 10^3 \gamma c t^{1/2} \qquad (18)$$

The time t_1 required for diffusion of a quantity sufficient for a saturated monolayer thus varies in inverse proportion to t^2. With $\gamma = 12$, t_1 is only 0.08 sec. at $c = 10^{-4} M$, but increases to eight sec. at 10^{-5}; thirteen minutes at $10^{-6} M$ and to eighty-nine days at $10^{-8} M$.

Actually we find, even without stirring, that the action of a dissolved salt is rapid at $10^{-6} M$ but very slow at $10^{-7} M$. Evidently convection currents produced by the spreading of the monolayer and thermal convection from slight temperature inequalities are very important factors in carrying solute to the surface.

Stirring the substrate solution gives the effect of a film of quiescent liquid of thickness l under the monolayer with an underlying solution of uniform concentration. When the solution is so concentrated that it is not appreciably depleted by the adsorption of a complete layer of ions on the monolayer we have

$$\sigma = nDt/l \qquad (19)$$

The following theory enables us to determine the number of ions adsorbed by stearic acid monolayers from data given by simple experiments in which successive films are skimmed off.

Consider a solution of concentration n_0 (molecules per cc.), in a trough of depth L, on which we spread a monolayer. A saturated film of adsorbed solute molecules will require σ_0/γ molecules per sq. cm., where σ_0 is the number of stearic acid molecules per sq. cm., and this will lower the concentration of the solute by an amount $\sigma_0/\gamma L$.

Let us now skim off the monolayer, apply a second monolayer, stir the solution under the monolayer for a time t_s and skim off the second layer. In this way we remove a total of N_2 monolayers before we find, by any test that we may apply, that the solute molecules can no longer be detected in the monolayers (or in the skims).

If n_0 is sufficiently great the first N_1 monolayers will be saturated with solute. From Eq. (19) we see that the concentration n_1 below which the monolayers are no longer saturated is given by

$$n_1 = l\sigma_0/\gamma Dt_s \qquad (20)$$

When $n < n_1$ the concentration decreases according to

$$\mathrm{d}n/\mathrm{d}N = -nDt_s/Ll \qquad (21)$$

Thus when $n_0 < n_1$ the relation of N_2 to n_0 is

$$N_2 = (Ll/Dt_s) \ln (n_0/n_2) \qquad (22)$$

where n_2 is the least concentration which gives a positive test for the adsorbed atoms.

When $n_0 > n_1$

$$N_2 = (\gamma L/\sigma_0)(n_0 - n_1) + (Ll/Dt_s) \ln (n_1/n_2) \qquad (23)$$

Thus a curve of n_0 as a function of N_2 gives an upper straight part of slope $\sigma_0/\gamma L$ and a lower part which gives a straight line if plotted on semi-log paper of slope $\mathrm{d} \ln n_0/\mathrm{d}N_2 = Dt_s/Ll$

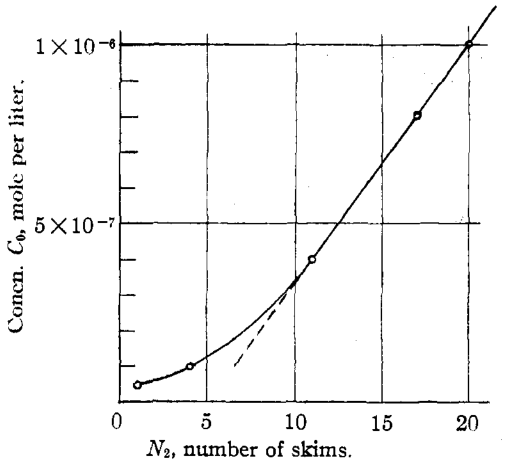


Fig. 1.—Adsorption of dissolved aluminum by stearic acid monolayers: C_0 is concn. of $AlCl_3 \cdot 6H_2O$ in moles per liter; N_2 is number of films skimmed to remove aluminum to recognizable end-point; capacity of trough, 350 cc.; surface area, 300 sq. cm.

Figure 1 gives the results of experiments with dilute solutions of aluminum chloride added to water at pH 5.8 in a trough 1 cm. deep. After each application of a stearic acid monolayer the solution was stirred by sweeping the quartz rod twenty times across the trough in one minute. The presence of aluminum in the film was detected by the modification in the crumple pattern and the crystallized monoskim which will be described later. The curve drawn in Fig. 1 is the theoretical line calculated by taking $D/l = 0.0038$ cm. sec.$^{-1}$, $t_s = 60$, $L = 1$, $\sigma_0 = 5 \times 10^{14}$, $\gamma = 12.4$.

The saturated film thus has only one aluminum atom for every twelve stearic acid molecules. If we take $D = 5 \times 10^{-6}$ we obtain $l = 0.0013$ cm., which indicates that this method of stirring is very effective in bringing the solution into close proximity to the monolayer.

The concentration c_2 which corresponds to the sensitivity of the crumple pattern test under the conditions of these experiments is 4×10^{-8} *M* and the concentration of aluminum in the film calculated by Eq. (19) is 5.5×10^{12} atoms cm.$^{-2}$, or only one atom of aluminum for every 90 of stearic acid.

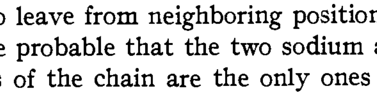
In subsequent experiments it was found that by stirring sixty times (three minutes) a concn. 2×10^{-8} *M* gave a recognizable amount of aluminum in the monolayer. With more effective stirring it should thus be possible to detect aluminum by the crumple pattern test in a solution 10^{-8} *M* in a trough 1 cm. deep.

We believe that nearly all other polyvalent cations at sufficiently high *p*H can be detected with equally great sensitivity by the alterations in the properties of stearic acid films.

We have not found effects characteristic of the anions ordinarily present in metallic salts. We have generally used chlorides, nitrates or acetates.

We have, however, found that the substance known as sodium hexametaphosphate or Calgon frequently has extremely great effects upon the properties of monolayers, particularly monolayers of stearates of divalent cations at high *p*H values. For example, at *p*H 9 a stearic acid film upon barium chloride, 10^{-4} *M*, is made extremely rigid by the addition of Calgon in a concentration of 10^{-6} *M* (molecular weight 615).

Our interpretation of the effect of Calgon is as follows. It has been suggested by Dr. J. A. Wilson[19] that Calgon is a polymetaphosphate (not necessarily six metaphosphate groups) consisting of long chains. The probable structure is thus



$$\begin{array}{ccccccccc} & & \mathrm{Na} & & \mathrm{Na} & & & & \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \\ \mathrm{Na} & \mathrm{O} & \mathrm{P} & \mathrm{O} & \mathrm{P} & \mathrm{O}\text{———}\mathrm{O} & \mathrm{P} & \mathrm{O} & \mathrm{Na} \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \end{array}$$

with the general formula $Na_2O(NaPO_3)_n$.

Sodium atoms tend to form free ions, but an atom which leaves the molecule at a particular point gives a negative charge to an oxygen atom and so makes it more difficult for other sodium atoms to leave from neighboring positions. It is therefore probable that the two sodium atoms at the ends of the chain are the only ones that become ionized. The negative charges on the two ends of the molecule by their repulsive action tend to hold the molecule straight. If, however, divalent ions such as Ba^{++}, are present in the solution, one of them would be attracted to one of the ends of the metaphosphate chain and would give it a net positive charge. This end of the molecule would tend therefore to attract the other negatively charged end so that the barium would close the link by forming a ring. The ring then would be uncharged so that one or two sodium atoms could leave it, leaving a net negative charge. The barium therefore now appears in the negative ion. This structure gives a satisfactory explanation of the remarkable property of Calgon in forming soluble complex negative ions from polyvalent cations. The pyrophosphate ($n = 2$) has too short a chain to form such rings and thus cannot exhibit properties of this kind.

This hypothesis also explains the action of Calgon in solidifying a barium stearate film. The replacement of sodium atoms in the metaphosphate chain by barium atoms adsorbed on the lower surface of the film gives powerful cross linkages between the molecules in the monolayer. This theory accounts for the fact that Calgon does not increase the rigidity of a stearic acid film when no barium is present or when more than enough Calgon is added to combine with the barium.

Further evidence that Calgon can be adsorbed onto a monolayer by positive ions or radicals is given by the fact that monolayers of heptadecyl amine on acid water (10^{-3} *N* hydrochloric acid) are made solid by Calgon.

Calgon is extremely useful in experiments with stearic acid monolayers on water when it is desired to remove disturbing traces of polyvalent cations originally present in distilled water, or coming from contamination by the trough. Thus the addition of 10^{-6} *M* Calgon to water (*p*H 4–9) in a trough of glass or metal holds the surface viscosity of a stearic acid monolayer at a constant value for long periods of time, whereas without the Calgon slow or even rapid changes will occur.

Potassium cyanide is another useful reagent to add in small quantity 10^{-6} *M* to eliminate troublesome effects of traces of copper in distilled water.

Spreading of Monolayers on Solutions

Drops of a benzene solution of stearic acid (3 parts per 1000) placed upon water at *p*H < 6.0 move slowly over the surface and remain small in area, shedding the stearic acid film from their

(19) J. A. Wilson, Jr., *J. Am. Leather Chem. Assoc.*, **32**, No. 3 (1937).

edges. There is, however, no perceptible contact angle at these edges.

With pH > 7, the drops of the benzene solution spread to relatively large areas (4 to 7 cm. diam.) and show marked interference fringes over a large part of their surface. The action is more vigorous and the spreading occurs much more rapidly than at lower pH.

Up to about pH 8.2 this type of spreading is not changed by addition of 10^{-4} M barium chloride. At pH $>$ 8.4, with barium the spreading becomes much more rapid and the benzene solution breaks up into great numbers of small droplets, distributed irregularly over the surface. These have an only momentary existence but it can be seen that each shows a relatively large contact angle against the surrounding monolayer. Evidently, there is a change in the character of the monolayer beyond pH 8.4 by which it tends to be oleophobic.

If more than enough of the benzene solution of the stearic acid is added than is needed to cover the surface of the monolayer, the drops suddenly stop spreading and show a contact angle which depends greatly upon the composition of the underlying solution. This angle is much smaller on acid than on alkaline water and is particularly great when barium is present at pH 9.0.

Organic substances may be used in the substrate which become adsorbed on the monolayer. We have long been familiar with the marked effects of tannic acid in the water in giving rigidity to many monolayers. Even a pure hydrocarbon oil has its interface made rigid by one part in a thousand of tannic acid, when calcium bicarbonate is present in the water. We have recently made studies of the adsorption of digitonin upon monolayers of cholesterol.[20,21]

Properties of Monolayers on Solutions

Many properties of monolayers are sensitive to dissolved substances and can be observed by simple means.

1. **Force–Area Curves (F–a).**—The area covered by a known weight of substance, spread as a monolayer, is measured at a series of different surface pressures F as given by a surface balance. Often great emphasis has been placed on the area per molecule (a) at $F = 0$ usually obtained from areas at higher values of F by linear extrapolation to $F = 0$. There seems to be no theoretical reason for attaching particular significance to a at $F = 0$. We have preferred to measure a at $F = 15$ or $F = 30$. These values of a are more easily correlated with the structure of the molecule.

2. **Electric Potential Measurements.**—This method has been used by many investigators for studying the changes in the condition of films when subjected to different pressures F. Schulman and Rideal[6] recently have studied the effect of dissolved organic substances. The method is a useful one which should throw much light on the nature of the adsorption of metallic ions. This method we have not used.

3. **Mechanical Properties, Viscosity and Elasticity.**—We find the two-dimensional viscosity of stearic acid monolayers to be particularly sensitive to traces of polyvalent cations. We have used three methods:

a. **Paper Strip Test.**—The viscosity of monolayers can be observed qualitatively by placing a strip of paper upon the film and blowing gently upon one end of it. If the film is liquid the paper rotates freely. With a solid film the strip acts as though it were frozen into the surface. It is easy to recognize intermediate degrees of viscosity and elasticity by this simple method.

b. **Indicator Oil Test.**—A very convenient test and one which is capable of detecting small increases in viscosity is made as follows: A minute drop of indicator oil on the end of a wire is placed on the monolayer which is originally under a pressure of 15 dynes/cm. or more. Then the pressure is completely released by the movement of the barrier which confines the monolayer. With a liquid or slightly viscous monolayer the indicator oil spreads to form a circular disk. A highly viscous film will usually tear so as to make a star-like figure. With a rigid or brittle monolayer the pressure of the oil causes one or more hair-line cracks to radiate out from the oil drop to the sides of the tray and the oil flows into these cracks and widens them.

In the case of fluid monolayers a sensitive measure of the viscosity can now be obtained (after releasing the pressure) by applying a second droplet of oil in the monolayer just a little distance outside the circular disk left by the first drop. If the monolayer has a viscosity equal to that of the indicator oil film the second drop will spread into a

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[20] I. Langmuir and V. J. Schaefer, THIS JOURNAL, **59**, 1406 (1937).

[21] I. Langmuir, V. J. Schaefer and H. Sobotka, *ibid.*, **59**, 1751 (1937).

second circular disk deforming the first disk by pushing into it the thin strip of intervening monolayer. If, however, the monolayer is more viscous than the first oil disk, then the second disk will expand mostly into the first disk instead of causing the uniform expansion of the monolayer which surrounds it.

A little experience with this simple test which can be made in a few seconds enables one to distinguish between a large number of degrees of viscosity or rigidity produced by increasing concentrations of salts in the substrate.

An excellent test for elasticity of monolayers, such as those of proteins,[12] is made as follows. A wire, bent into the form of a 1-inch (2.5-cm.) square, with a wire handle perpendicular to the plane of the square, is coated with a thin layer of indicator oil and is then lowered horizontally into the monolayer confined between barriers, so as to cut out a square. On releasing the pressure by a movement of the barrier the indicator oil expands to form a colored film. If the monolayer is a rigid solid, the square outlined by the oil retains its shape and size. If it is an elastic solid it remains square but increases in size when the pressure is decreased. With a liquid monolayer the square loses its shape and mixes with the oil if subjected to a slight air current.

c. **Absolute Viscosity and Elasticity Measure.**—The coefficient of surface viscosity of a liquid monolayer may be defined by the equation

$$F_s = \mu_s \, dv/dx \qquad (24)$$

where F_s is the shearing stress (dynes/cm.) in the film produced by a velocity gradient dv/dx.

The coefficient of surface elasticity E_s (for shear) of an elastic solid monolayer is similarly defined by

$$F_s = E_s \, ds/dx \qquad (25)$$

where E_s is the deformation produced by the shearing stress F_s.

These quantities μ_s and E_s can be measured by the motions of a platinum disk,[22] preferably about 2 cm. in diameter, which is suspended by a fine tungsten wire (0.03 to 0.06 mm. diam.) from a torsion head mounted above the trough, so that the disk lies in the surface of the water. The torsion head is so arranged that it can be turned quickly through any one of a series of fixed angles such as 30, 90, 180°, etc., by means of a pointer moving between stops or pins inserted in holes in a plate. The floating disk is provided with a pointer or mirror and a scale for measuring angles, and has a pair of brackets which can hold a rod having a known moment of inertia. After the water surface around the disk has been cleaned, a monomolecular film is applied and is compressed to a given value of F.

By turning the torsion head the disk can be made to oscillate and the damping can be used to measure the viscosity of a liquid monolayer. With a disk of radius a, at the center of a circular area of film of radius b, the torque transmitted through the film is equal to

$$\varphi = 2\pi\mu_s r^3 d\omega/dr \qquad (26)$$

where ω is the angular velocity of a ring of film of radius r. For films of sufficiently high viscosity we may neglect the frictional drag exerted on the film by the underlying layers of water so that φ in Eq. (26) is independent of r. By integration we can thus calculate μ_s in terms of the damping coefficient p (torque φ per unit of angular velocity, ω_a, of the disk):

$$\mu_s = Hp \qquad (27)$$

where H is a constant of the apparatus given by

$$H = (1/a^2 - 1/b^2)/4\pi \qquad (28)$$

When p is small the disk oscillates with gradually decreasing swings. If λ· is the natural logarithm of the ratio of successive swings, we have (for $\lambda < 1.2$)

$$p = (2/\pi)(MD)^{1/2}\lambda(1 + \lambda^2/10)^{-1/2} \qquad (29)$$

where M is the moment of inertia of the moving system and D is φ/Θ_D or the torque exerted by the wire per radian of angular displacement of the disk.

If p is large compared to the value for critical damping $2(MD)^{1/2}$, then

$$p = D/(d \ln \Theta_D/dt) \qquad (30)$$

where Θ_D is the angular displacement of the disk during relaxation.

When the monolayer is an elastic solid E_s is given by

$$E_s = DH(\Theta_H/\Theta_D - 1) \qquad (31)$$

where Θ_H and Θ_D are, respectively, the angular displacements of the torsion head and the disk.

In experiments to measure μ_s and E_s for monolayers by these methods we have used a disk 1 inch (2.5 cm.) in diameter (a = 1.27 cm.) in a rectangular tray 10 cm. wide. We see from Eq. (25) that H depends very little on b if b is large compared to a. Therefore it should make very little difference if we replace a circular tray by a

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[22] In a recent note [R. J. Myers and W. D. Harkins, *J. Chem. Phys.*, **5**, 601 (1937)] two other types of apparatus have been described for measuring the viscosities of monolayers.

rectangular one. We assume $b = 6$ cm. as an effective radius of the tray and thus get $H = 0.047$.

With this apparatus we first determine T_0, the (complete) period of oscillation of the disk in air and measure also λ_0 with a known value of M. We then calculate D by

$$T = 2\pi(M/D)^{1/2} \qquad (32)$$

and p_0 by Eq. (29).

Similar measurements with the same suspension wire are made with the disk on a clean water surface determining T_W and λ_W.

The values of M calculated from D and T_W by Eq. (32) are greater than those found for the disk in air because of the water under the disk carried along with it by friction. If we assume that a layer of water of thickness h is carried with the disk, the increment in M due to this cause is equal to

$$M_W = \pi/2\ \rho h_1 a^4 = 1.57\ h_1 a^4 \text{g. cm.}^2 \qquad (33)$$

Using a disk 1 inch (2.5 cm.) in diameter ($a = 1.27$ cm.) with a mounting giving an oscillation period of six and one-half seconds, we find by experiments with a trough containing water with no monolayer $M_W = 0.19$ when the water is 0.2 cm. deep and 0.26 for depths between 0.5 and 1.0 cm. The corresponding values of h_1, calculated by Eq. (33), are 0.047 and 0.065 cm. Since M_W probably also depends slightly on T and λ, it is desirable when using the oscillation method to load the disk with a rod having a sufficient moment of inertia to make M large compared to M_W.

From λ_W and $M + M_W$ we then calculate p_W by Eq. (29). Part of this, p_0, is due to air friction, etc., so that $p_W - p_0$ is the damping coefficient due to the water. Calculation shows that for laminar flow between two disks separated by a distance h_2, small compared to their radius, we should have

$$p_W - p_0 = (\pi/2)\mu_W a^4/h_2 \qquad (34)$$

where μ_W is the viscosity of water.

Our experiments with the one-inch (2.5-cm.) disk have given $p_0 = 0.089$ for the damping coefficient in air and $p_W = 0.435$ (g. cm.^{2} sec.$^{-1}$) on clean water with depths ranging from 0.2 to 1.0 cm. By Eq. (34), putting $\mu_W = 0.010$ at 20°, we find $h_2 = 0.11$ cm. This small value of h_2 compared to the depth of the water is probably the result of centrifugal force which produces an outward flow of the rotating layers of water under the disk drawing up underlying non-rotating liquid along the axis.

The frictional damping coefficient p_W is equivalent to an apparent surface viscosity of 0.021 (g. sec.$^{-1}$) which we have subtracted from values of μ_s given by Eq. (27) from experimental data for p with monolayers. Increasing M also makes it possible to extend the range of values of p that can be measured by the oscillation method.

Table I gives a summary of data on the absolute viscosities of a few of the monolayers measured. Other data will follow in a subsequent paper.

4. Crumple Patterns.—If a monolayer on a water surface is crushed slowly between two barriers while being observed by the naked eye using strong transverse illumination (the bottom of the trough should be black), certain patterns of lines or fine points are seen which are highly characteristic of certain salts dissolved in the water.

For example, with a monofilm of stearic acid on pure water (pH 5.8) fine lines appear on the monofilm when the area of a condensed film ($F = 30$) is decreased 10%. If the movement of the barriers is stopped, these lines disappear, but reappear when the barriers are again set in motion. When the monolayer is reduced to about half its original area, the whole surface has a fine-grained, star-like but nearly uniform or isotropic appearance. On further compression, the light scattered from the surface increases steadily in intensity until finally a white scum of folded layers of monofilm is formed, which can be skimmed off onto a narrow glass slide.

If the same experiment is repeated after having added ammonia to pH 9, the crumple pattern does not appear until the area has been reduced 60% or more. The skim then scatters much less light than before.

Very minute traces of impurities in the benzene used in making the stearic acid solution cause the appearance of irregular streaks or whorls in the crumple pattern when spread on pure water at pH 5.8. Dr. Blodgett has found that one part of oxidized automobile oil in four million parts of a benzene solution containing 0.1% stearic acid will alter the compression pattern in this manner. This test is thus a sensitive one also for detecting non-volatile impurities in substances such as benzene.

Merck C. P. benzene was redistilled and those fractions were used which when tested by making an 0.001 solution of stearic acid in benzene showed the fine-grained isotropic star-like pattern described above.

TABLE I

ABSOLUTE SURFACE VISCOSITIES OF MONOLAYERS ON WATER SOLUTIONS

F = 15 dynes cm.$^{-1}$ D = 4.5. pH > 5.8 buffered as described in paper. M = 131.8. T = *ca.* 34 sec.

Substance spread	Trough	pH	Age of H_2O, min.	Age of film, min.	μ_s, g. sec.$^{-1}$
Stearic acid	Glass	5.8	5	3	0.002
Stearic acid	Glass	5.8	16	14	.002
Stearic acid	Glass	5.8	50	48	.016
Stearic acid	Glass	5.8	80	3	.011
Stearic acid	Glass	5.8	5	3	.002
Stearic acid	Glass	6.8	5	3	.04–0.08
Stearic acid	Glass	8.2	5	3	.5
Stearic acid	Glass	8.2	12	10	1.0
Stearic acid	Glass	9.0	15	3	2.6
Stearic acid	Bakelite	9.0	5	3	0.042–0.70 collapse
1 × 10^{-5} M Calgon					
Stearic acid	Bakelite	9.0	10	3	.042
3 × 10^{-5} M Calgon					
Stearic acid	Bakelite	9.0	17	3	.056
Stearic acid	Bakelite	9.0	30	10	.627
1 × 10^{-4} M Calgon					
1 × 10^{-5} M KCn					
Stearic acid	Bakelite	9.0	40	3	.078
Stearic acid	Bakelite	9.0	60	10	.700
Stearic acid	Bakelite	9.0	70	22	.767
Stearic acid	Rh plate	5.8	5	3	.016
Stearic acid	Rh plate	5.8	13	11	.12
Stearic acid	Rh plate	5.8	18	16	.57
Stearic acid	Rh plate	5.8	35	2	.16
Stearic acid	Rh plate	5.8	46	13	1.7
Stearic acid	Rh plate	5.8	58	25	13.0
1 × 10^{-4} M $BaCl_2$					
Ba stearate	Glass	5.5	5	2	0.31
Ba stearate	Glass	5.8	9	6	.77
Ba stearate	Glass	5.8	14	11	1.34
Ba stearate	Glass	6.9	21	2	1.4
Ba stearate	Glass	6.9	25	6	2.3
Ba stearate	Glass	6.9	28	9	8.5
Ba stearate	Glass	8.2	40	5	0.70
Ba stearate	Glass	8.2	46	11	.70
Ba stearate	Glass	9.0	59	2	.80
Ba stearate	Glass	9.0	68	11	.85
Cetyl alcohol	Glass	5.8	150	3	.32
Cetyl alcohol	Glass	5.8	5	3	.38

When various salts are added to the water (10^{-5} M) many types of crumple patterns are observed. For example, copper and lead at pH 6 give "banded crumple patterns" which are characterized by bands of weakness parallel to the barriers, along which nearly all the crumpling takes place. Gradually, as the compression is increased, more bands appear. The same type of crumple pattern is observed with copper at pH 9. With lead, however, at pH 9, the crumple pattern is almost invisible and the collected skim retains much water.

Calcium, magnesium, cadmium and aluminum at pH 6 give crumple patterns consisting of fine parallel transverse folds. Zinc, barium, mercuric ions, manganese, iron, cobalt and nickel at pH 6 give somewhat similar patterns except that the lines of folding are no longer straight and parallel but are wave-like or irregular with their general direction running parallel to the barriers. At pH 9, however, the lines of folding again become straight and regular like those observed with calcium and magnesium at pH 6. With most of these elements the lines of folding appear to a marked degree only when the compression is carried to about half the original area.

The addition of 10^{-6} M Calgon to a solution of 10^{-4} barium at pH 9 changes the crumple pattern from that characteristic of barium to one which resembles the banded crumple pattern of copper and aluminum.

5. Examination of Skim.—After observation of the crumple pattern, the monolayer is crushed by moving the barriers to about one-quarter of an inch (6 mm.) from each other. Then this crushed film can be skimmed off the surface with a narrow strip of glass, transferred to a microscope slide and covered with a cover-glass. After heating above the melting point of stearic acid (70°), the slide is allowed to cool while being observed under a polarizing microscope. If the film consists of pure stearic acid it crystallizes suddenly, the crystallization starting from a point which acts as a nucleus. These crystals are birefringent. If metallic soaps are present, due to adsorption of metallic cations from the water, the crystallization is a more gradual process, often giving Liesegang rings and leaving portions which are not doubly refracting.

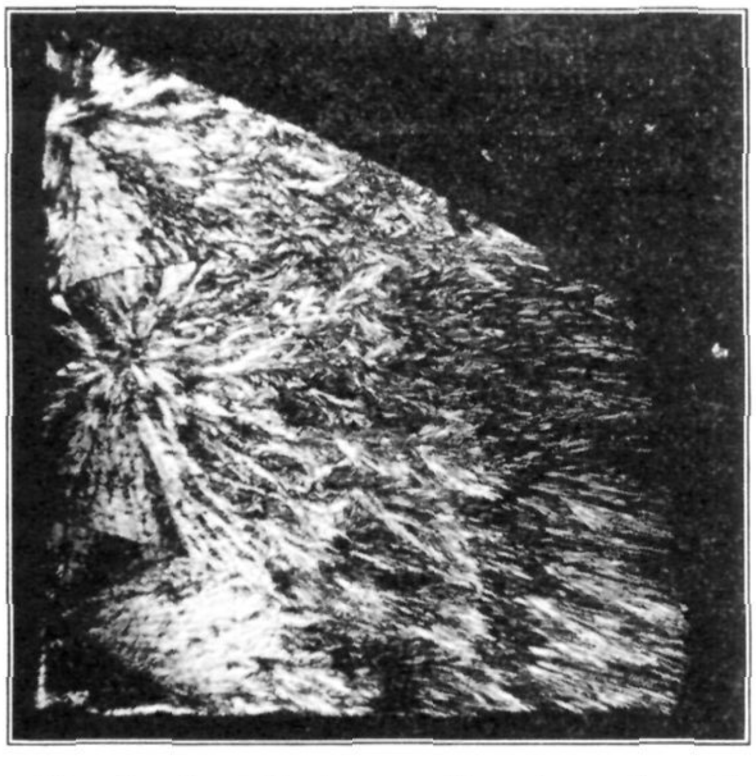

Fig. 2.—Crystallized monoskim of stearic acid; microphotograph taken with crossed polarizing screens; quartz distilled water; pH, 5.8; T, 25°; water stirred 60 times.

This test is extraordinarily sensitive to the presence of metallic cations in the solution. Microphotographs of the crystallized monoskims were taken by Mrs. C. B. Brodie, of this Laboratory. Figure 2 shows the result obtained with stearic acid on pure water. Figure 3 shows the skim obtained with water to which $AlCl_3 \cdot 6H_2O$ was added in a concentration 2×10^{-8} M. In both cases the water beneath the film was stirred sixty times. If all the aluminum were concentrated in the film, there would only be one atom of aluminum for every thirty-one molecules of stearic acid.

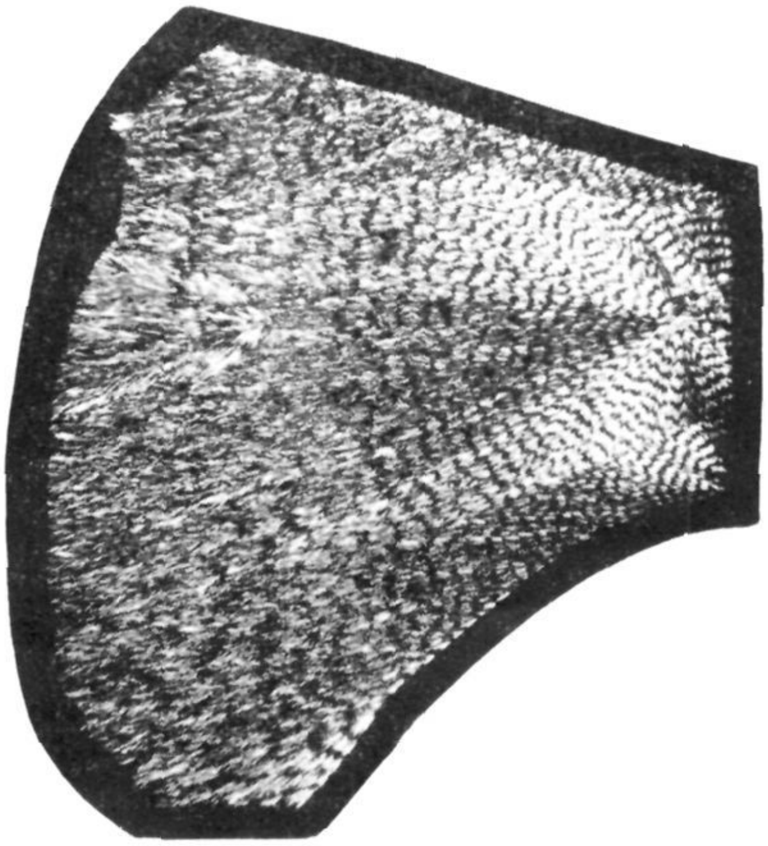

Fig. 3.—Crystallized monoskim of stearic acid + Al; microphotograph taken with crossed polarizing screens; quartz distilled water; $2 \times 10^{-8} M$ $AlCl_3 \cdot 6H_2O$; pH, 5.8; T, 25°; solution stirred sixty times.

A very low concentration of copper in the water, such as 5×10^{-8} M $CuCl_2 \cdot 2H_2O$, gives a skim which when collected upon porcelain and heated to 100° has a distinct green color. Amounts of Calgon, from a solution of 10^{-6} M concentration, which are adsorbed on a barium stearate film at pH 9, give skims which develop a charred appearance when heated to about 300°, which is quite different from the appearance obtained without Calgon.

Monolayers of many organic substances give skims which when observed under the polarizing microscope show very characteristic crystals after heating to definite temperatures and cooling.

By transferring the skim to a platinum surface and igniting it, a residue is left which contains the metallic constituents of the monolayer. These can then be examined spectroscopically, or by other microchemical methods.

Summary

The technique and apparatus have been described for making qualitative or quantitative determinations of the adsorption of dissolved salts from aqueous solutions by a surface monolayer of an insoluble substance.

The absolute viscosities of stearic acid and barium stearate monolayers on water having various *p*H values have been listed. These show progressive changes due to adsorption of impurities. The equations and the apparatus used for measuring the viscosity or elasticity of insoluble monolayers have been given.

The modification of a crystallized monoskim of pure stearic acid by the adsorption of aluminum from water containing one part of aluminum in two billion parts of water has been shown by photographs. A melted monoskim of stearic acid colored by copper adsorbed from water containing one part of copper in three hundred million parts of water was described.

Simple methods for the visual observation of the modification of pure stearic acid monolayers caused by minute concentrations of impurities in water which produce a change in the crumple pattern and crystallized monoskim have been described, together with the detection in a similar way of non-volatile impurities in volatile substances such as benzene.

Equations have been given for the rate of diffusion of dissolved substances through water to an insoluble monolayer on the surface and a method described for greatly accelerating the rate of arrival at the surface.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Equilibria in Solutions of Cadmium and Zinc Oxalates[1]

BY WILLIAM J. CLAYTON AND WARREN C. VOSBURGH

The conductivity data of Scholder[2] for a number of oxalates in water solution have been interpreted by Money and Davies[3] in terms of simple ionization. Scholder had explained the abnormally small conductivities entirely on the basis of complex ion formation, but Money and Davies consider this to play only a small part. Among the oxalates in question were those of cadmium and zinc, for which the simple ionization constants are given as 1.3×10^{-4} and 1.3×10^{-5}, respectively, at 18°.

This paper presents the results of a further investigation of equilibria in solutions of cadmium and zinc oxalates by electromotive force and solubility methods. The solubility products at 25° were determined by an electromotive force method, and the solubilities of the two oxalates were determined in cadmium and zinc sulfate solutions, respectively, and in potassium oxalate solutions. From the experimental data, the concentrations of simple ions, undissociated molecules and complex ions in the various solutions have been calculated. The results are in agreement with the conclusions of Money and Davies.

Materials.—Cadmium and zinc oxalates were prepared by slow addition of 0.1 *M* cadmium or zinc sulfate solution to an equal volume of 0.11 *M* oxalic acid solution. In the preparation of the zinc oxalate, the oxalic acid solution was seeded with crystals formed by mixing a small portion of the two solutions.

All other salts used were recrystallized at least once from water.

Mercury was purified by treatment with mercurous nitrate solution and distillation.

Cadmium and zinc amalgams were prepared by electrolysis of cadmium or zinc sulfate solution with a mercury cathode and with a C. P. stick of cadmium or zinc, as anode. The cadmium amalgam contained about 10% cadmium and the zinc amalgam about 5% zinc.

One sample of quinhydrone was obtained from the Eastman Kodak Company and others were prepared by the method of Biilmann and Lund.[4] Further treatment of the quinhydrone is described below.

Apparatus.—A Leeds and Northrup Type K potentiometer was used for the electromotive force measurements. A group of five saturated Weston cells was used as a reference standard.[5] These cells were compared with a similar set of cells that had been checked by the National Bureau of Standards, and the value assigned in this way agreed within 0.01 mv. with the value that had been assigned previously by comparison with newly made cells. The standard cells were kept in an oil-bath at 25 ± 0.02°.

For the temperature control of the experimental cells

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[1] A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1937.

[2] Scholder, *Ber.*, **60**, 1527 (1927).

[3] Money and Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[4] Biilmann and Lund, *Ann. chim.*, [9] **16**, 339 (1921).

[5] The standards were cells 353–356 and 496 which have been used as standards for several years. See Vosburgh and Elmore, THIS JOURNAL, **53**, 2822 (1931).