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OVERTURNING AND ANCHORING OF MONOLAYERS*

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IN some studies of the mechanism of the flotation process made several years ago[1] monolayers of oleic acid were spread on water, and by a dipping process were deposited upon solid surfaces of glass, platinum, mica, calcite, sphalerite and galena. With each of these solids no monolayer was deposited on the down-trip into the water, but on the up-trip the surface came out of the water initially wet and on top of the water film there was a monolayer of oleic acid. After the draining out or evaporation of the water film the hydrophilic groups in the oriented oleic acid molecules were brought into contact with the solid surface to which they adhered more or less firmly, depending on the nature of the solid. Repeated dipping into a clean water surface, dusted lightly with talc, proved that for all the surfaces except mica little or none of the oleic acid monolayer escaped onto the water.

Two methods were used for detecting and studying the properties of these deposited monolayers: observations of the lubricating properties and of the contact angles given by drops of water placed on the surface.

The monolayers on the solid surfaces had an enormous effect upon the static friction of small glass sliders placed on the surface. On glass without the film the sliding angle was over 60°, but this was reduced to about 6° by the monolayer.

Drops of water placed upon a clean surface of any of these solids spread over the surface, wetting it completely, thus giving a zero contact angle, θ. The clean surfaces are therefore hydrophilic. After the oleic acid monolayers had been deposited, the surfaces became hydrophobic and the contact angles depended greatly upon the character of the underlying solid. With mica the angle was 18°, 45° for glass, 65° for platinum, 70° for calcite, 82° for sphalerite and 86° for galena.

Mica behaved differently from the other substances

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* Address of the vice-president and chairman of the Section of Chemistry, American Association for the Advancement of Science, Indianapolis, December 28, 1937.

[1] I. Langmuir, *Trans. Faraday Soc.*, 15: 62, 1920, reprinted in *G–E Rev.*, 24: 1025, 1921.

in that a considerable part of the oleic acid monolayer deposited on mica was given up when the mica was dipped into clean water, as shown by the talc test. If the mica covered by the monolayer was repeatedly passed through a stream of water it became wetted nearly as easily as a surface of freshly split mica. The hydrophobic character of oleic acid monolayers on the surfaces of the other substances, however, was not appreciably changed by passages through a stream of water.

According to a theory which I had previously developed[2,3,4,5] the surface tension and presumably the contact angles characteristic of a surface involve only short-range forces and depend primarily on the nature of and arrangements of the atoms which form the actual surface and not directly upon the nature of underlying molecular layers. From this viewpoint because of the orientation of the molecules we might be led to suppose that the upper surface of oil films on solid bodies should always consist of CH_2 or CH_3 groups, so that the surface properties of all the films would be similar.

There is, however, an important distinction between the case of an oil film covered by a water drop and a surface layer of a pure organic liquid. The water drop on the film tends to draw the active groups to itself and so cause a reorientation of the molecules. In the case of oleic acid there are two active groups in the molecule; the carboxyl group and the double bond. We may assume that on galena, with its strong field of force the active groups are held so firmly that water can not cause any appreciable fraction of them to change their orientation. Thus the surface of the oleic acid film on galena consists almost entirely of hydrocarbon groups and the contact angle with water is only slightly less than that observed on solid paraffin ($\theta = 110°$). With a monolayer on glass, on the other hand, the presence of an overlying drop of water may bring some of the active groups to the upper surface of the film, so that the water spreads over this surface much more easily than over paraffin, giving a much lower contact angle.

This theory also readily explains the marked difference between the contact angles of an advancing and a receding water surface on glass covered by an oleic acid monolayer. The advancing surface is continually moving onto a surface having few hydrophilic groups, while at the receding edge of the drop the water must peel back from the surface on which there are many hydrophilic groups produced by the reorientation of some of the polar molecules.

Another factor which may cause contact angles to depend upon the nature of the solid under the monolayer is that the spacing of the molecules in monolayers on solids may often be dependent primarily on the surface lattice of the solid, whereas with films on liquids the molecules are able to arrange themselves largely without reference to the structure of the underlying liquid. As a result, the films on solids are ordinarily not in stable equilibrium; many molecules are crowded into spaces too small for them, while others occupy unnecessarily large areas. Even in our early experimental work with films on solids we found that the results were much more irregular and depended much more on slight differences in the previous histories of the films than in the case of monolayers on liquids.

The clean surfaces of glass and the fresh cleavage surfaces of the minerals used in these studies were both hydrophilic and oleophilic, being completely wetted by water or by Petrolatum. However, if very pure Petrolatum was applied first it was found that this was completely displaced from the surface by a drop of water. This displacement could be prevented by very minute traces of fatty acids dissolved in the Petrolatum, for then a hydrophobic adsorbed monolayer was formed between the solid and the hydrocarbon and this could not be removed even by washing with benzene.

Dr. K. B. Blodgett in 1933[6,7,8,9] developed a method of building successive layers of stearates of divalent elements or even of pure stearic acid. Films produced in this way are remarkable in that they are both hydrophobic and oleophobic.

According to Bartell[10] the contact angle θ_R made by a drop of any organic liquid R on a solid can be calculated by the equation

$$\gamma_R \cos \theta_R = (12.8 - \gamma_{RW})K + 65.2 \quad (1)$$

where γ_R is the surface tension (dynes cm^{-1}) of the liquid (against air), γ_{RW} the interfacial surface tension between the liquid and water and K is a parameter (K_{n3} in Bartell's nomenclature) which is characteristic of the solid only. The contact angle θ_W for a drop of water can be calculated by the same equation if we place $\gamma_{RW} = 0$ and replace the subscript R by W.

Let us consider the application of this theory to drops of water and of Petrolatum (Squibb's) on barium stearate films. Previous measurements[11] have given $\gamma_R = 31.7$; $\gamma_{RW} = 53.0$ and $\gamma_W = 72.8$. Eq. (1) then gives

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[2] I. Langmuir, *Met. Chem. Eng.*, 15: 468, 1916.

[3] I. Langmuir, *J. Am. Chem. Soc.*, 39: 1848, 1917.

[4] I. Langmuir, *Colloid Chem.*, 1: 525, 1926, edited by Jerome Alexander.

[5] I. Langmuir, *Chem. Rev.*, 6: 451, 1929.

[6] K. B. Blodgett, *J. Am. Chem. Soc.*, 56: 495, 1934.

[7] K. B. Blodgett, *J. Am. Chem. Soc.*, 57: 1007, 1935.

[8] K. B. Blodgett and I. Langmuir, *Phys. Rev.*, 51: 964, 1937.

[9] K. B. Blodgett, *J. Phys. Chem.*, 41: 975, 1937.

[10] F. E. Bartell and L. S. Bartell, *J. Am. Chem. Soc.*, 56: 2205, 1934.

[11] I. Langmuir, *J. Chem. Phys.*, 1: 756, 1933, see p. 762.

$$\cos \theta_R = 2.10 - 1.29 \text{ K} \quad (2)$$

$$\cos \theta_W = 0.90 + 0.18 \text{ K} \quad (3)$$

According to these equations, hydrophobic solids ($\theta_W > 0$) are those for which $K < +0.56$ while solids are non-wettable by Petrolatum or oleophobic ($\theta_R > 0$) only if $K > +0.85$. Solids whose values of K lie between 0.56 and 0.85 are oleophilic and hydrophilic. This theory, however, denies the existence of any solids which are both oleophobic and hydrophobic.

Now there are numerous surfaces (clean glass, metals, etc.) which are in fact both hydrophilic and oleophilic and these fit in with Bartell's theory. However, the barium stearate multilayers are hydrophobic and oleophobic, as experiments give for water $\theta_W = 90°$ and for Petrolatum $\theta_R = 55°$. If we substitute these values into Eqs. (2) and (3) we obtain $K_R = +1.19$ and $K_W = -5.0$, whereas by Bartell's theory K_R and K_W should be equal.

Bartell's theory was based on observations of contact angles given by 5 liquids on 16 solids. The values of K ranged only from -0.81 to $+0.91$. The discrepancy shown by the stearate multilayers is therefore a very great one, and proves that Bartell's theory can not be generally applicable.

Y-Films: When barium stearate films are built up from stearic acid spread on a solution containing 10^{-4} M $BaCl_2$ 2×10^{-4} $KHCO_3$ at pH 6.8, monolayers are deposited both when the film is lowered into the bath and when it is raised out of the bath. Films of this type we call Y-films. The layers deposited on the down-trip we call A-layers and those formed during the up-trip we call B-layers. Thus Y-films consist of alternating ABAB . . . layers. On the water surface the stearic acid monolayer or H-layer[12] is undoubtedly oriented with the carboxyl group down, and therefore presumably the A-layer has the carboxyl group on the side away from the plate while the B-layer is oppositely oriented so that the tail or hydrocarbon end of the molecule forms the actual surface. Thus in the multilayers the barium atoms should be located in layers with spacings twice the length of the stearate molecule. X-ray examination of the films proves in fact that the spacings of the planes containing the barium atoms is 48.8 Å, while optical measurements prove that the thickness per stearate layer is 24.4 Å.

When water drops are placed upon a barium stearate Y-multilayer, built from H-layers on a solution containing 10^{-4}M $BaCl_2$, 2×10^{-4}M $KHCO_3$ (pH 6.8), the contact angle is 90°. If a drop of water weighing 60 mg is placed on such a prepared plate and this is tilted 25°, the drop begins to move. By decreasing the angle the motion is made to stop, and then the angle at the receding edge is 82° and at the advancing edge 110°. If a drop of Squibb's Petrolatum is used in a similar way the initial angle is 53°, the receding angle 29° and the advancing angle 55°.

The observed hydrophobic character of the Y-multilayers, whose outermost layer is a B-layer, lends support to the view that the molecules are oriented so that the hydrocarbon tail is uppermost. It would seem that direct evidence of the orientation of the A-layer could be obtained by depositing an A-layer on a down-trip and then sweeping off the remaining H-layer by moving a barrier across the water surface so as to avoid the deposition of a B-layer on the up-trip. When this is done, however, it is found that the B-layer escapes onto the water surface. This can be proved not only by observing the motion of talc dusted on the water but also by the direct optical determination of the thickness of the film on the plate by the methods that have been developed within the last few years.[8, 9, 13, 14]

The fact that the film goes back onto the water surface indicates that the force between the water and the A-film is greater than that between the A-film and the underlying B-film, and thus gives support to the belief that the side of the A-film which is furthest from the chromium plate is hydrophilic. We have not yet found any way to anchor the hydrophobic side of the A-layer so as to be able to bring out into the air a hydrophilic A-layer of barium stearate.

It seems remarkable that a substance like Petrolatum should peel off from barium stearate Y-layers when it is considered that the orientation of the uppermost B-layer is such that the actual surface consists entirely of hydrocarbon. The probable explanation is that the molecules are so tightly packed into an area of about 20 Å^2 per molecule that only the CH_3 groups at the ends of the molecules are exposed on the surface. The properties of CH_3 may well be so different from CH_2 that a liquid consisting mostly of CH_2 does not wet a surface consisting entirely of CH_3.

X-Films: If the pH of the bath from which barium stearate monolayers are deposited onto the chromium plate is raised to about 9, it is found under certain conditions that monolayers are deposited only during the down-trip (A-layers). In this case the plate emerges from the water in a dry condition after each up-trip, giving a contact angle of about 90° with the water, whereas when Y-films are formed at pH 6.8 the contact angle at which the water recedes from the plate on the up-trip is about 50°.

Proof that a film goes on during the down-trip and none on the up-trip is furnished by observing the

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[12] The need for a terminology and a symbol for a monolayer of an insoluble substance on water is met by calling such a monolayer an H-layer.

[13] I. Langmuir, V. J. Schaefer and D. M. Wrinch, SCIENCE, 85: 76, 1937.

[14] I. Langmuir, V. J. Schaefer and H. Sobotka, *J. Am. Chem. Soc.*, 59: 1751, 1937.

motion of talc particles placed on the H-layer near the plate. Optical determinations of the thickness of the plate show that the increment of thickness is about 26 to 28 Å per round trip, while with Y-layers it is 48.8 Å per round trip.

There is usually some difficulty in starting the building of X-films. Thus, if after a number of layers of Y-type have been built from a solution at pH 6.8, the pH is changed to 9.0, the first 3 to 4 dips continue to give Y-layers. Then, usually near the edges of the plate and especially near the bottom edge, X-films begin to form. After one or two more dips uniform X-films are deposited over most of the area of the plate.

Dr. Blodgett[9] has found that with solutions of certain pH values it is possible to build either X- or Y-films, depending upon the length of time the film is held under water. If after each down-trip the slide is held 10 sec or more under water, no B-layer is deposited on the following up-trip, so that X-films are built. If, however, the plate is immediately raised out of the solution after the down-trip, a B-layer is deposited on the up-trip so that Y-layers are formed. There appears to be a marked difference of composition between the X- and Y-films. The Y-films are easily skeletonizable by dipping for a few seconds in benzene; this dissolves out the free stearic acid, which may be present to the extent of 10 to 40 per cent., depending on the pH, leaving the thickness of the film unchanged but greatly reducing the refractive index, since each stearic acid molecule is replaced by a void. X-films, however, undergo no appreciable change when dipped into benzene, indicating that there is no appreciable amount of free stearic acid, the film presumably consisting wholly of neutral barium stearate.[15] This increase in barium content occurs spontaneously during the time the film is under water.

Dr. Blodgett has found that X-films of lead stearate are formed from H-layers of stearic acid on 10^{-4}M $PbCl_2$, pH 5.6. If 5×10^{-6}M $SnCl_2$ or 10^{-4}M $FeCl_2$ + 5×10^{-3}M KI, pH 5.4, is added good Y-films of lead stearate can be built. When H-layers of arachidic acid of doubtful purity on 10^{-4}M $PbCl_2$, pH 5.6, are deposited on a chromium plate good Y-films result. In all these cases the Y-films are skeletonizable in benzene, whereas the X-films are not.

Since the X-films consist of a series of A-layers, we should expect them to be so oriented as to give a hydrophilic surface. However, measurements of contact angles obtained with water and Petrolatum on X-films give results practically identical with those on Y-films. We must conclude therefore that in some way the hydrophilic groups in the molecule have been drawn below the actual surface. The practical identity of properties suggests in fact that the deposited A-layer has acquired the same orientation as a B-layer. Thus the molecular layer has overturned, presumably while immersed in the solution.

The structure of X-films is not yet definitely known. There are many apparently contradictory features to be reconciled. X-ray determinations of the spacing between layers of barium atoms in X-films have been made by Holley and Bernstein[16] who find the same spacing as in Y-films. This implies an alternating orientation of successive layers. There is nothing, however, in the method of deposition of X-films to suggest a periodicity corresponding to two round trips.[17]

Porter and Wyman[18] have shown that the potential of the surface of a Y-film on chromium with respect to the underlying metal stays practically constant at about + 0.2 volts as the number of layers in the Y-film increases. With X-films, however, the potential increases linearly with the number of layers, about 70 mv per layer. Porter and Wyman consider this as evidence for internal polarization of the film such as would be expected if all the layers had similar orientation, a result in conflict with Holley and Bernstein's measurements.

Porter and Wyman in a second paper[17] show that the total potential of a composite film consisting of X- and Y-layers is brought nearly to zero by the addition of one or two pairs of Y-layers, whereas one or two X-layers raise the potential nearly as high as if the whole film were built of X-layers. These results seem to indicate that the potentials of the X-layers are not due to internal polarization but are caused by a surface electrification or a kind of frictional electricity, generated by the recession of water from the hydrophobic surface during an up-trip. In the case of Y-films there is no such recession from a surface, for the water between the B-layer and the underlying A-layer is forced out by an attraction between the hydrophilic groups of layers by a kind of zipper action.[13] There is thus none of the slipping of one surface over another which would seem to be needed for the development of frictional electricity.

If the potentials of the X-films are due to a surface charge, the potential should increase in proportion to the number of layers. There is then no evidence from the experiments against an alternating arrangement for the layers inside the X-films. The uppermost

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[15] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 58: 284, 1936.

[16] C. Holley and S. Bernstein, *Phys. Rev.*, 52: 525, 1937.

[17] (Private communication from E. F. Porter and J. Wyman, Jr.) In their second paper, *J. Am. Chem. Soc.*, 60: 1083, 1938, Porter and Wyman give evidence that during the early stages of the building of X-films the electric potentials and the contact angles show alternating increases and decreases, indicating a periodicity corresponding to two dips.

[18] E. F. Porter and J. Wyman, Jr., *J. Am. Chem. Soc.*, 59: 2746, 1937.

layer, however, presumably always has an orientation similar to that of a B-layer.

The suggestion has been made by Porter and Wyman[17] that X-films with an odd number of layers have structures like Y-layers, with alternating orientations throughout the film.

When one more A-layer is deposited, making the total number even, this new layer overturns to give an orientation like that of the B-layers of a Y-film, so that now the outer two layers have similar orientation. When a second A-layer is deposited, giving again a film with an even number of layers, it is then necessary that the new layer and the one below it shall both overturn, in order to reestablish the alternating orientation characteristic of the odd number of layers.

A convenient way of representing the structures of built-up films is to employ the small (l.c.) letters p and q. Two layers which have molecules oppositely oriented so that their "heads" face one another are thus shown as pq, while qp represents two layers having the "tails" of the molecules in contact.[19] If we adopt the convention of placing P, which represents the solid plate at the left with the symbols for the successive layers to the right of it, Porter and Wyman's suggested structures of X-films (in air) are: P qp qp q for 5 layers, P(5), P qp qp qq for P(6) and P qp qp qp q for P(7).

An odd-numbered layer, such as the outside layer in P(5), must originally have been deposited as a p-layer (A-layer), but overturned to give a q-layer before being brought out into the air. It remains as a q-layer in P(6) and P(7).

An even-numbered layer, such as the outside layer in P(6), starts out as a p-layer when deposited, overturns to give a q-layer before being brought out into the air, and overturns again, back to a p-layer, in P(7) probably at the time when the outside layer of P(7) overturns.

Thus the q-layer which constitutes the outside layer of an X-film in air overturns to give a p-layer when another layer is placed on it, *unless the heads of the molecules in the q-layer are in contact with* (or anchored by) *the heads of an underlying p-layer.*

The slight alternations observed by Porter and Wyman[17] in potentials and contact angles are probably to be explained as due to a less complete orientation of the outside q-layer (even number of layers) than when the outside q-layer is more firmly anchored by an underlying p-layer (odd number of layers).

Whatever the structure of X-films may ultimately turn out to be, it seems that overturning of layers must be involved in their formation.

Skeleton Films: The comparative stability of skeleton films of lead, cadmium or barium stearate which contain as much as 40 per cent. of voids seems to indicate an extraordinary rigidity for the hydrocarbon chain. To form a void or hole in a solid substance such as a barium stearate layer should require an energy roughly equal to the heat of evaporation of a molecule, which in the case of stearic acid must be very large. Thus the collapse of a skeleton film should involve a large decrease of free energy and should be an irreversible process.

Professor Edward Mack, Jr., has given me some models of hydrocarbon chains in which the carbon atoms are represented by aluminum spheres 1.54 cm in diameter, connected by rod-shaped axes about which the spheres can be rotated freely. The scale of the model is such that 1 cm corresponds to 1 Å. Hemispheres of a diameter of 2.0 cm with their centers in positions corresponding to the hydrogen nuclei determine the distance of nearest approach of hydrogen atoms in neighboring hydrocarbon molecules.[20] When this model of the hydrocarbon chain is placed on a flat surface it is possible to arrange the carbon atoms in a zigzag which corresponds to the crystal structure of stearic acid. The molecule as a whole then has roughly the form of a rectangualr prism, 4.3 × 3.9 Å with a cross-section which corresponds to 17 Å^2, only a little less than the 19.2 Å found for the cross-section of hydrocarbon chains in crystals of hydrocarbons. As long as the molecule rests on a flat surface it acts as a rigid body. If, however, it is lifted off the flat surface, it can be rolled up nearly into a sphere or into a great variety of other shapes.

In barium stearate films the hydrocarbon chains have their axes perpendicular to the plane of the film and each is probably surrounded by 6 neighboring chains. If half the film consists of stearic acid and this is removed by skeletonization, each molecule of barium stearate remains in contact with about 3 out of the 6 neighboring molecules. The free rotation around the carbon-carbon linkage takes place about an axis inclined 35° from the axis of the hydrocarbon chain. The presence of neighboring molecules can thus prevent free rotation so that the molecules are held in a rigid form and collapse is prevented.

Mechanism of Overturning: The rigidity of the hydrocarbon chains, illustrated by the properties of skeleton films, is in striking contrast to the mobility required for the overturning of molecules or even

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[19] To avoid confusion due to overturning it seems necessary to use A and B as symbols to denote only the *method of deposition* (down-trip and up-trip) and not the orientation of layers. Thus Y-films are PBABAB . . . AB and X-films are PRAB . . . AA, although the orientation of their layers may perhaps be the same. In Y-films the A- and B-layers correspond respectively to p and q layers but because of the overturning there is no such relationship in the X-films. The orientation of p layers may be described as *exotropic* (having the head turned out) while that of q layers is *endotropic* (head turned in).

[20] Edward Mack, Jr., *J. Am. Chem. Soc.*, 54: 2141, 1932.

whole layers of molecules within solid multilayers. It is inconceivable that rigid molecules could turn end over end in these films. However, the models of Dr. Mack indicate that a hydrocarbon chain if freed from the constraint of its neighbors can bend into a U-form in which the two legs of the U, and the semicircular bend between them, have a total cross-section of only 40 Å^2. Thus in the q-layer of barium stearate which constitutes the outside layer of an X-film, a single barium atom joins two adjacent stearic radicals, forming a kind of U. By a kind of ring-around-the-rosy motion the U-shaped molecule is changed into a C-shaped molecule by the gradual shortening of one leg and the lengthening of the other, whose free end bends down to follow the receding short end. In this way, by a continuous process, the whole molecule of barium stearate turns from a U into an inverted U and so the barium changes its position to the opposite side of the monolayer. The overturning of the monolayer thus depends upon free rotation about the carbon-carbon bonds but for each molecule requires a space no greater than that of a prism of cross-section of 20 Å and a length of 25 Å.

Although the stability of skeletonized films shows that the hydrocarbon chains are sometimes extraordinarily rigid, the extreme rapidity with which such skeletons are formed by dipping stearate films in benzene for 1 second proves very high internal mobility. During this short time benzene molecules must penetrate into the film to a depth of 100 or 200 barium stearate layers (5,000 Å) and displace the stearic acid molecules from their positions. Skeletonization is possible (at a rate 100 times slower) even if the Y-film is covered by a "blanket film" of 20 layers of neutral barium stearate which itself is not skeletonizable.[13]

Overturning of B-Layers by Thorium Nitrate. The A-layers deposited on the down-trip during the building of a Y-film are exotropic and therefore, if aluminum chloride or thorium nitrate is introduced into the solution after the down-trip, we should expect the polyvalent cations to combine with the carboxyl groups and so join them together that the A-layer can no longer escape onto the water surface during the up-trip. Thus we should produce a hydrophilic A-layer. These predictions were completely verified by experiments.[21]

Subsequently it was found[22] that a B-layer could be conditioned in this way by solutions of polyvalent cations just as well as an A-layer, the film being made hydrophilic. The B-layer of a Y-film is endotropic, and so there is no obvious reason for expecting interaction of the film with cations in the solution since only the hydrocarbon parts of the molecules are exposed. We must conclude that the B-layer has overturned and been changed from a q- to a p-layer. We may assume that thermal agitation causes individual molecules to overturn from time to time, the number in reversed orientations at any one time being extremely small, although a given molecule may overturn many times per second. If the plate is now dipped into thorium nitrate, the molecules which do overturn spontaneously become anchored by the thorium ions and are so prevented from returning to their original orientation.

Dr. G. H. A. Clowes has reported that barium stearate films can be conditioned by uranyl salts at pH 6 but at pH 5 or 7 this treatment does not render the surface hydrophilic. We have found that the Y-barium stearate films, rendered hydrophilic by the 10^{-3}M uranyl nitrate solution at pH 6, remain so if washed with distilled water in equilibrium with the CO_2 of the air at pH 5.8, but immediately become hydrophobic if washed with distilled water which contains less CO_2, pH 6.6. However, a few drops of water of pH 5.8 again render the surface hydrophilic. Apparently this action can be repeated indefinitely. We have found a few other cases (sodium desoxycholate) where very slight changes of pH may change conditioned surfaces reversibly from a hydrophilic to a hydrophobic condition. Perhaps these are due to overturning of the surface layers. The phenomenon is one which deserves much further study.

Protein Films: Protein H-layers can be deposited on plates covered by barium stearate films either as A-layers or as B-layers. Many proteins, for example zein and gliadin, and others in less degree, give hydrophobic films when deposited at surface pressures $F < 10$ dynes/cm, but at higher pressures the surfaces become hydrophilic. There is no appreciable difference, however, between A- and B-films in this respect. This seems to indicate that the A- or B-films can readily overturn in response to the conditions to which they are exposed. For example, if a drop of water is placed on the surface, the hydrophilic side chains are moved to face the water, whereas when an oil drop is placed on the surface the hydrophobic groups move into contact with the oil.

The reactivities of the protein monolayers also seem to be the same whether the layers are of A or B types. Presumably, however, the reactivities and other properties should depend on orientation. It was therefore desirable so to anchor the hydrophobic or the hydrophilic groups in the protein film that these can not overturn. If a B protein monolayer is deposited on a stearate plate conditioned with thorium nitrate, the hydrophilic groups in the protein become anchored to the thoria. Such a surface is much more highly hydrophobic than a protein film deposited directly onto barium stearate.

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[21] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 59: 1406, 1937.

[22] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 59: 1762, 1937.

By conditioning a stearate plate with thorium and then treating with sodium desoxycholate, the surface is rendered extremely hydrophobic. The desoxycholic acid has a great affinity for hydrocarbons, and thus when a B-layer of protein is deposited on a surface conditioned with desoxycholate the hydrophobic parts of the protein are anchored, while the hydrophilic groups are left free to form the actual surface. Protein films prepared in this way were found to be hydrophilic.

The chemical activities of urease monolayers[23] deposited and anchored in these two ways were found to differ markedly in their ability to convert urea into ammonia. The hydrophobic surface of urease adsorbed on the surface conditioned with thoria was very reactive, whereas the hydrophilic urease adsorbed on desoxycholate showed no appreciable activity.

Anchoring of Fatty Acid Monolayers on Glass and Chromium. In depositing the initial B-layer of stearic acid on the clean glass or chromium, preparatory to the building of multilayers, Dr. Blodgett[7] found that the pH of the water and the presence of certain cations were of great importance in determining the adhesion of the monolayer to the plate. In the early work on monolayers of oleic acid on the surfaces of minerals[1] ordinary tap water had been used and no study of the effect of the pH was made. With the assistance of Mr. C. N. Moore I have recently undertaken experiments with monolayers of oleic and stearic acids on glass and chromium plates.

A microscope slide cleaned in a sulphuric-chromic acid mixture, washed thoroughly with distilled water and dried was coated with oleic acid or stearic acid in several ways and was then tested by placing a drop of water on the surface and observing the contact angle. B-layers of oleic or stearic acid, deposited from H-layers on distilled water, were displaced from the glass surface by a drop of water placed on the glass, leaving the glass completely wetted by water $\theta = 0$). On the other hand, if a portion of a dry glass surface was moistened with 0.1 M sodium hydroxide or barium hydroxide solution, and this was then thoroughly washed with distilled water, the oleic or stearic acid B-layers were hydrophobic and adhered firmly to the glass on those parts of the surface which had been treated with the alkali. In the case of the surface which had been treated with sodium hydroxide the contact angle against water was 20°, while the surface treated with barium hydroxide gave 40°. An essentially similar result was obtained when the cleaned glass plate was washed with Schenectady city water which contains the equivalent of about 40 parts of $MgCO_3$, 72 of $CaCO_3$, and 77 $CaSO_4$ per million.

We also tried applying liquid oleic acid directly to the glass. This film was completely displaced by water unless the glass had previously been treated with alkali. Stearic acid, however, when melted on the clean glass surface forms drops which show a large contact angle against the glass (oleic acid on glass gives a practically zero contact angle). The glass so treated was hydrophobic and gave with water a contact angle of about 20°.

By dipping dry clean glass surfaces into dilute solutions of oleic or stearic acid in benzene, monolayers of the acids were adsorbed from *solution*. The layers formed in this way, which we shall call S-layers, were immediately displaced from the surface by the addition of a few drops of water, giving a hydrophilic surface. Treatment with sodium hydroxide or barium hydroxide before applying the benzene solution gave hydrophobic surfaces.

In each of the foregoing cases which gave a hydrophobic surface the contact angle was not lowered by repeatedly passing the plate through a stream of running water. It was also not markedly altered by repeated dipping into pure benzene or by heating to 100° C.

A series of tests were made with films of oleic and stearic acid applied in various ways to surfaces of chromium plated brass which had been thoroughly cleaned by polishing with shamva. An oleic acid S-layer applied from a benzene solution and a B-layer both gave contact angles of $\theta = 55°$ when a drop of water was placed on the surface. There was a considerable hysteresis, however, for when the slide was tilted the angle at the advancing edge of the drop rose to about 90°, while at the receding edge it fell to 40°. Drops of Petroleum gave advancing angles of 3° and receding angles of 0°, so that the surfaces were oleophilic.

Molten stearic acid on chromium draws up into drops and leaves on the metal a monolayer which shows a contact angle for water $\theta > 90°$ and about 30° for Petrolatum. When clean chromium was treated with a dilute solution of stearic acid in benzene and was then washed in pure benzene, an S-layer was left which gave a contact angle of 70° with water. A drop of Petrolatum gave a contact angle of about 5–10° and a receding angle only slightly greater than zero; that is, the oil drop peeled back from the surface extremely slowly with a hardly perceptible contact angle.

The S-layers of the fatty acids on glass or chromium and the B-layers of oleic acid on glass were oleophilic, whereas barium stearate Y- or X-films are oleophobic, giving $\theta = 53°$.

The difference between the S- and B-layers of stearic acid is probably due to a regular close-packed arrangement of the molecules deposited from an H-layer, while the molecules of stearic acid that diffuse to the surface

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[23] Paper by I. Langmuir and V. J. Schaefer to appear in the June number of the *J. Am. Chem. Soc.*

in the benzene solution to form the S-layer are far less regularly spaced. The contact angles θ we have been discussing are measured by placing drops of liquid on the surface of a monolayer on a solid. This angle serves as a measure of the work of adhesion W given by

$$W = \gamma\ (1 + \cos\theta)$$

where γ is the surface tension of the liquid of the drop.

Zipper Angles: There is another angle, which we shall call the *zipper angle,* z, that measures the adhesion of a B-layer for an underlying surface. For example, a clean chromium slide is immersed in clean water and then an H-layer of stearic acid is spread on the water. The water appears to peel back from the slide as this is slowly withdrawn from the water, leaving the slide dry but with a B-layer which has been deposited on its surface. Actually, however, the water is forced out[13] from under the B-layer by attractive forces exerted by the polar groups of the B-layer upon the underlying polar atoms of the chromium surface—a kind of "zipper-like" action. The force of gravity is entirely inadequate as a cause of this phenomenon. The angle z is conveniently measured by withdrawing the slide from the water in an inclined position (its surface inclined from the horizontal by the angle z) and so altering z that the water surface remains horizontal right up to the line of contact with the plate. The angle is readily measured within about 10°.

Oleic or stearic acid B-layers deposited on glass from pure water gives $z = 0$; *i.e.,* the water is not forced out from under the B-layer. Such a B-layer is described as a *hydrous* B-layer, as it is separated from the underlying plate by a relatively thick layer of water (several microns at first). On standing a few minutes in the air the water film evaporates and the B-layer (then called a dehydrous B-layer) then comes into contact with the glass. If the glass has been previously treated with alkali, this B-layer becomes firmly anchored to the glass and can not be displaced by water or dissolved off by benzene.

Recent experiments have shown that B-layers of oleic, stearic and arachidic acids deposited on clean glass from H-layers on distilled water are hydrous, $z = 0$, even if the pH is adjusted to values from 4 to 9 by HCl, $NaHCO_3$ or NH_4OH.

B-layers of these acids deposited on a Shamva-polished chromium surface give zipper angles $z = 50$ to 60°, so that the plates emerge dry. These B-layers are firmly anchored to the chromium plates and are not displaceable by water or soluble in benzene.

CONCLUSION

The structure and surface properties of monolayers and multilayers are frequently determined by the orientations of individual molecular layers, but under certain conditions a layer may undergo an almost instantaneous reversal of orientation. This overturning may alter the chemical and physical properties.

It seems probable that the overturning of molecular layers may be a phenomenon of considerable biological significance. If the monolayers contain dipoles or ionic charges as well as hydrophobic and hydrophilic groups, the overturning of the layer may cause large changes of electric potential. Conversely, change of potential or of chemical composition of the liquid on one side of a membrane may cause an overturning of one or more of the monolayers and so change the properties of the film. The phenomenon of overturning may perhaps help explain the mechanism of the propagation of nerve impulses.

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[24] I. Langmuir, *J. Franklin Inst.,* 218: 143, 1934, see p. 156.

SCIENTIFIC EVENTS

REPORT OF THE TRUSTEES OF THE BANTING RESEARCH FOUNDATION

A TEN-YEAR period has elapsed since the first group of grants was made by the trustees of the foundation. During this period grants have been made annually in accordance with the charter to the Department of Medical Research under Sir Frederick Banting; and also 184 grants have been made to 110 individuals distributed throughout Canada as follows: Brandon College 1; Dalhousie University 10; McGill University 18; Queen's University 2; University of Alberta 3; University of British Columbia 1; University of Manitoba 13; University of Saskatchewan 2; University of Toronto 56; University of Western Ontario 5.

During the year 1936–37, 28 workers received grants from the foundation and 24 papers have been published as the result of grants made in this or previous years. The following brief comments may be made on the grants made during the year:

B. F. Crocker, University of Toronto: A new method is being employed for the study of the process of digestion in dogs and satisfactory progress is being made. Dr. J. C. Goodwin, University of Toronto: A further payment was made in order to have a technical analysis of the report made on the observations made in regard to the relationship between the inter-racial origin of parents and the progress of labor. Dr. E. R. Grant, McGill University: On the cause of otosclerosis. Dr. A. W. Ham, University of Toronto: A valuable research was carried out on the changes in joint cartilage produced by vitamin C. Mrs.