that these words are perfectly acceptable, more writers would employ them. This would make for greater simplicity and often for greater clarity in setting down laboratory directions.

So unfamiliar are alkalify, alkalinize and alkalize that many instructors have made a habit of correcting students of elementary chemistry who have used them. Yet "alkalize" has had recognized standing since 1749.

This year a greater number of students than average have sought to use "alkalize" in place of more round-about expressions of the same idea. Probably their practice was inspired by the advertisements of a certain laxative mixture, where the word is used rather loosely. But whatever the source of the stimulus, there is no reason why alkalize, alkalinize or alkalify should not have wider usage. Rather than reprove the students for using these words, we might well follow their example.

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SPECIAL CORRESPONDENCE

FOURTH ANNUAL TRI-STATE (ILLINOIS, IOWA, WISCONSIN) GEOLOGICAL FIELD CONFERENCE

GEOLOGISTS and students of geology in the three above-mentioned states participated in the annual tri-state field conference on October 31 and November 1. The conference was held this year in Calhoun and Jersey counties in central western Illinois. It was conducted by A. H. Sutton, University of Illinois, assisted by J. Marvin Weller, Illinois State Geological Survey.

The conference was attended by 117 persons, who traveled in 35 cars. Geologists from eleven universities, colleges and state surveys of the three states and representatives of six oil companies operating in Illinois were present. Invited guests of the conference included six persons from Washington University, St. Louis, Mo., one from Oklahoma A. and M. College and the manager of the Alton, Ill., *Telegraph*. The geology of the stops was described in a mimeographed log and a blue-print map, furnished each participant at the beginning of the conference. In addition each car was supplied with quadrangle topographic maps of the area visited.

The conference began at Hardin, Calhoun County, at 9 A.M. on Saturday. The first day's trip included eight stops in Calhoun County. The stratigraphic section studied during the day is summarized below: *Mississippian:* St. Louis, Spergen (Salem), Warsaw, Keokuk, Burlington, Sedalia (Fern Glen), Chouteau, Hannibal, Louisiana, Saverton. *Devonian:* Cedar Valley. *Silurian:* Joliet, Kankakee, Edgewood. *Ordovician:* Maquoketa, Kimmswick, Decorah, Plattin, Joachim, St. Peter.

Good exposures of all these formations were visited for examination and fossil collecting. Contacts between most adjacent formations were observed. The Cap-au-Gres faulted monocline was studied and discussed. G. E. Ekblaw, Illinois State Geological Survey, explained the origin of the terraces along Illinois River and gave a brief summary of the Pleistocene and recent history of the area. W. H. Twenhofel, University of Wisconsin, and J. E. Lamar, Illinois State Geological Survey, discussed problems of the St. Peter sandstone, comparing the formation in this area with that in the northern portion of the Mississippi Valley.

The annual dinner and general meeting was held at the Stratford Hotel in Alton, Ill., on Saturday night and was attended by 103 persons. No formal papers were presented, but geologic problems of the area were discussed. Dr. Ekblaw presented a more detailed summary of the geologic history than had been given earlier in the day.

On Sunday, November 1, the trip covered portions of Jersey County. Several of the stratigraphic units which had been examined the previous day were seen again, and the Cap-au-Gres structure was studied in more localities. The conference closed at noon on Sunday at an exposure of Pleistocene varved lake deposits which were made in a pond adjacent to the margin of the Illinoian Ice.

The conference will be held next year in Wisconsin under the leadership of Professor F. T. Thwaites, of the University of Wisconsin.

A. H. SUTTON

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SPECIAL ARTICLES

BUILT-UP FILMS OF PROTEINS AND THEIR PROPERTIES

MANY proteins can exist in water as large spherical molecules, but they can also spread on water surfaces, giving elastic solid monomolecular films having great two-dimensional compressibility. The present paper describes experiments made to determine whether the methods[1, 2] developed in this laboratory for studies

[1] I. Langmuir, *Jour. Franklin Inst.*, 218: 143, 1934.

[2] Katharine B. Blodgett, *Jour. Am. Chem. Soc.*, 57: 1007, 1935.

of monolayers of higher fatty acids are applicable to monolayers of proteins.

We have been able to transfer monolayers of protein from a water surface onto solid surfaces, where their thickness can be measured by optical methods and many new properties can be observed.

As a solid substrate upon which to build up such films we have found it preferable to use a surface already covered with a number of layers of barium stearate obtained by the method described by Dr. Blodgett.[2] For example, we use a plate about the size of a microscope slide consisting of highly polished chromium plated brass. If 37 to 47 layers of barium stearate are placed upon this plate, the interference colors observed with polarized light at large angles of incidence are so sensitive to changes in thickness of the film that an increment of 3×10^{-8} cm produces noticeable change of color. A single monolayer of protein thus produces a very striking color change. A further development of Dr. Blodgett's technique, using monochromatic light and a photocell to determine the relative reflectivities of adjacent steps, should make it possible to measure variations in thickness much less than 10^{-8} cm.

A monomolecular film of protein may be transferred to a solid surface prepared in this way as follows: The surface of distilled water in a tray is cleaned by scraping with a barrier. A narrow strip of paper is placed upon the water near one end of the tray. A platinum wire, to which a few particles of protein, such as egg albumin or pepsin, are attached, is made to touch the surface of the water and the monomolecular film spreads out from these particles, pushing ahead of it the floating paper strip. A small drop of purified oleic acid is then applied to the water on the other side of the paper strip, so that a surface pressure of about 30 dynes per cm acts upon the protein film. The paper strip indicates the boundary between the protein film and the oleic acid film.

MONOFILMS

A single monolayer of protein may now be transferred to the prepared plate in two different ways. In the first method, which we shall denote as Method A, the plate, held in a vertical plane, is lowered into water. The movement of the paper barrier toward the plate proves that the protein film is being transferred to the plate. The plate is then kept immersed in the water while the protein film is removed from the surface by scraping and by blowing any residual film to the opposite end of the tray, where it may be confined behind a barrier. The plate, when raised out of the water, comes out wet, whereas if the protein film had not been placed upon the plate, the plate would have shed water when it was withdrawn. After allowing the surface film of water to evaporate, examination of the plate with polarized light at angles near grazing incidence shows that the part of the plate to which the protein film has been applied differs markedly in color from the original stearate film. Comparing the color with that of stearate films having a known series of steps, it is seen that the thickness of a film of egg albumin obtained under these conditions is about 20×10^{-8} cm.

The second method of applying the protein film, which we shall call Method B, consists in lowering the prepared plate vertically through a clean water surface, then applying the protein film as before and raising the plate out through this film. The motion of the paper strip again shows that a protein film is transferred to the plate. However, since the plate comes out wet and at first shows no interference colors, it is evident that the protein film is not yet in contact with the plate but lies on a water film several microns in thickness. As the water dries, the protein film becomes attached to the substrate. This film has about the same thickness as that obtained by Method A.

It is remarkable that, although the prepared plate (without a protein film), lowered into clean water and withdrawn, comes out dry, it is covered by a thick water layer if the plate is withdrawn from water upon which there is a protein film. If before drying the slide, it is lowered into the water, the movement of the paper barrier shows that the protein film goes back on the water surface, notwithstanding the 30-dyne pressure exerted by the oleic acid. These phenomena at first suggest that the protein film acts through the water film, a distance of several microns, upon the stearate film on the plate and so modifies it that it remains wet. A closer examination of the process by which a stearate film sheds water proves, however, that this depends upon the presence of a line of contact between the water-air, the water-stearate and the air-stearate interfaces. This one-dimensional contact line is the seat of the phenomenon. The forces acting along this contact line which are enormously more intense than any that can be exerted by gravity on a water film of a few microns' thickness produce a "zipper-like" effect in closing up the space available for the water film.

The action of the protein film by which it prevents the shedding of the water is thus to be interpreted as evidence that the work of adhesion between the protein film and the stearate film is not sufficient to give a sufficiently strong zipper action. The film of water is then about twice as thick as that occurring on a *clean* glass slide withdrawn from water, since the water film, descending only by gravity, is confined in the first case

between two stationary surfaces (the plate and the protein film), while in the case of the glass slide one surface of the water is free.

MULTIPLE FILMS

We have found it possible to build up multiple protein films under certain conditions. To classify the types of film obtained let us use P to denote the plate, R for the hydrocarbon surface upon it (barium stearate layers with CH_3 radicals forming the surface), A and B for protein layers produced by Methods A and B, respectively. Thus, for example, PRAB denotes a prepared plate upon which there is an A film covered by a B film.

PRAB FILMS

By dipping a plate into water covered by a protein film, withdrawing it and drying the water film, two layers of protein can be transferred to the plate. The thickness indicated by the color change is approximately twice that of a single layer. With pure water as the liquid substrate we have not succeeded in repeating this process to build up films having the structure PRABAB. If a PRAB film is lowered into pure water or into water covered by a protein film, even under 30 dynes/cm pressure, the B film is ejected from the plate on to the water surface. This is evident from the motion of the paper strip. The loss of the B-layer from the plate when it is dipped into the water has also been proved by withdrawing the plate through a clean water surface, drying it and examining the color.

The addition of zinc chloride to the water (10 mg per liter) prevents the separation of the B from the A layer and makes it possible to continue adding AB layers indefinitely giving PRABABAB ... films. In this way 30 layers were built up without difficulty and the thickness as indicated by color increased in proportion. We believe that very accurate measurements of the thickness of the films can be made in this way. They should also be useful for study of structure by x-ray and electron diffraction.

PRBBB ... FILMS

Successive B films can be built up, even without adding zinc salts, by lowering the plate into clean water and withdrawing it through a protein film. The plate always comes out wet and the new layer must be dried on before the next one is applied. The dried-on B-films are not ejected from the plate either on immersing or withdrawing the plate.

PRBAB FILMS

After a single B film has been applied and dried, the plate takes up an A film if it is lowered through a protein film. When the plate is withdrawn through a clean water surface, a PRBA film is formed; if withdrawn, through a protein layer, PRBAB is formed. Further than this, we have not been able to go without adding zinc salts, since the last B film is ejected if the plate is lowered into water. We have not succeeded in producing PRAAA films, but with difficulty have obtained imperfect PRAA films.

All the types of films which we have been able to build using oleic acid pressure (30 dynes/cm) can be built without appreciably greater difficulty, using castor oil (about 15 dynes/cm) as piston oil.

PROPERTIES OF THE PROTEIN FILMS ON SOLIDS

The foregoing observations lead to the conclusion that there are some essential differences between A layers and B layers. For example, B layers which lie upon A layers are ejected on to the water surface on immersing the plate in water (in absence of zinc salts); whereas B layers upon B layers are not ejected. The methods used to form the layers indicate that A layers are turned upside down (inverted) in their formation, whereas the B layers are not inverted. Thus the outer surfaces of the A and B layers should be hydrophilic and hydrophobic, respectively.

The adhesion of B or A layers to a PR substrate is such that dipping into water does not cause the removal of the layer.

The fact that A and B layers preserve their identity after immersing in water indicates that they can not readily turn over. This supports the theory that they consist of a two-dimensional network rather than polypeptide chains.

The outer surfaces of both A and B layers are wettable by water and by hydrocarbons such as hexadecane, petrolatum, benzene and hexane, and show no striking differences in contact angles. If either A or B layers are partly covered by petrolatum and then a drop of water is placed on an adjacent place on the layer, it can be observed on tilting the plate that the water displaces the hydrocarbon. This action is considerably more marked with an A film than with a B film, and gives some evidence for the greater hydrophilic character of A.

The most striking evidence that the outer surface of A and the inner surface of B are predominantly hydrophilic is furnished by the ejection on to the water of a B layer, which rests upon an A layer. This action is undoubtedly caused by the affinity of this hydrophilic interface for water.

STEARATE FILMS BUILT UPON PROTEIN FILMS

When a prepared plate PR, partly covered by an A or B film, is lowered into water containing Ba salts covered by a stearic acid film, under 30 dynes pres-

sure, it is seen that the water rises on the PRA or PRB film (contact angle of about 40°), whereas it is strongly depressed on the PR portions (contact angle far greater than 90°). When the plate is withdrawn through the stearate film on the water, the PR portions come out dry (with two additional stearate layers), while the PRA or PRB portions are wet. After drying, the color indicates that two stearate layers have been added on top of the protein film. If the plate is again lowered and raised through the stearate film on the water all portions of the plate come out dry and two more stearate layers have been added to the whole plate. In this way it has been possible to sandwich any number of single protein layers between layers consisting of even numbers of stearate monolayers.

Permeability of Protein Films

The composition of built-up barium stearate films depends upon the pH of water.[3] With strongly acid water, pH = 3, the films are nearly pure stearic acid, whereas with pH = 9 they are nearly pure neutral barium stearate. At pH = 6.5 the barium content is about half of that in barium stearate.

Dr. Blodgett has found that the films of neutral barium stearate remain unchanged in color after immersing in benzene, but when the barium content is decreased by using a lower value of pH during formation of the film, the free stearic acid can be rapidly dissolved out of the film by benzene. Her measurements of refractive index of such films have shown that the change of color produced by immersing a part of the film in benzene is due to a change of refractive index of the film and not due to a change of thickness. Stearate films, from which free stearic acid has been removed, may be called *skeleton films,* since the barium stearate lattice remains unchanged, while the molecules of free stearic acid are removed, very much as the water molecules in a zeolite crystal can be removed without altering the silicate lattice.

If a drop of a liquid hydrocarbon such as petrolatum or hexadecane is placed upon a skeleton film, it shows a lower contact angle than upon a film of neutral barium stearate; but the drop can still be made to move about on the plate without wetting it. The drop, however, leaves behind it a trail of the same color as the portions of the stearate film which have not been dipped into benzene. Thus the hydrocarbon immediately returns into the holes left by the removal of stearic acid and restores the refractive index to its original value, 1.49 (values as low as 1.25 may be obtained with skeleton films).

Vapors of octane and decane brought into contact with skeleton films also cause the refractive index to rise to 1.49, but when the source of vapor is removed, evaporation of the hydrocarbon causes a gradual return to the original lower value characteristic of the skeleton. A large number of non-volatile organic substances in benzene solution can be introduced into the holes of a skeleton film by dipping the film into such a benzene solution, and the extent to which the film takes up these substances can be quickly and accurately determined by the color changes. Such films thus constitute molecular sieves which may be used to determine the sizes, shapes and surface affinities of organic molecules.

It has also been possible to place a few layers of neutral stearate upon fifty layers of acid stearate and to measure the rate at which benzene removes free stearic acid through the insoluble neutral layers. In a couple of hours practically all the free stearic acid (equivalent to 15 layers) can be removed from 50 layers of acid stearate through 20 layers of neutral stearate, whereas without the addition of the neutral layers the removal would have been nearly complete in 1 or 2 minutes.

The foregoing technique may be applied in several ways to study the permeability of protein monolayers to various organic substances.

Method C: A protein film (A or B) may be applied to a prepared plate of acid stearate and if desired covered by 2 or 4 additional layers of acid stearate. Then the plate is immersed in benzene for definite time intervals, after each of which the color is observed. Petrolatum, the vapor of a volatile hydrocarbon or a benzene solution of an organic substance, is then applied to the plate and the color changes are noted. The advantage of covering the protein film by additional stearate layers is that a hydrocarbon liquid does not wet the film. Without such additional layers, the hydrocarbon wets the protein layer and forms such a thick layer of liquid that interference colors are not obtained.

Method D: A protein film may be applied directly upon a skeleton film and the taking-up of hydrocarbons or other substances may be studied.

In measurements made by Methods C and D with monolayers of egg albumin we have found that protein films are very much more impermeable (of the order of 100-fold) to benzene, stearic acid and the lower aliphatic hydrocarbons than are equally thick films of neutral barium stearate. Protein films applied under 30 dynes/cm are more impenetrable (of the order of 10-fold) than similar films applied under 15 dynes/cm. Protein films seem to be almost wholly impervious to petrolatum molecules, for a skeleton film $PR_{45}AR_2$, over which a petrolatum drop has been made to pass,

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

undergoes no greater change of color than would be expected from the hydrocarbon that enters the two upper layers R_2. Without the A the color returns to that of the unskeletonized film.

Several observations on the rate of removal of stearic acid by benzene have given indications that an A film is somewhat more impermeable than a B film.

Effect of Surface Pressure on the Thickness of Protein Films

The area covered by a film of egg albumin on water decreases to one half when the surface pressure is raised from 15 to 30 dynes/cm. The thickness observed with $PR_{41}B_5$ applied under 15 dynes pressure agrees well with the color of $PR_{41}B_4$ applied under 30 dynes/cm pressure. Thus the thickness of the two kinds of films transferred to the solid differs in the ratio 1.0 to 1.25, while on the water surface the ratio is 1 to 2.

This difference suggests that strong forces of adhesion act upon the protein film on the solid to hold it flat so that the spacing is determined by the C-C and C-N linkages. On the other hand, the presence of the many hydrophilic groups in the protein molecules enables the lower surface of the protein monofilm on water to become wavy and so get into better contact with water. This waviness would account for the marked compressibility on water and the relatively smaller compressibility when forced to lie flat on a solid surface.

We have made some preliminary experiments to devise methods for studying protein films at the interface between water and hydrocarbon. A piece of egg albumin attached to a platinum wire was brought into contact with the interface between a lens of petrolatum and the underlying water. The lens was rapidly deformed in shape and in places made so thin that interference colors were obtained. The duplex films[2,4] thus produced are remarkably stable, as there is no tendency for the petrolatum to peel back, leaving a monolayer of protein on the water. The method just described is apparently not suitable for the formation of a uniform duplex film. A substance such as egg albumin, however, can be introduced as a water solution under the petrolatum. As the spherical molecules come into contact with the film, they appear to unfold into monolayers at the interface. Duplex films produced in this or other ways should afford a useful way of studying interfacial protein films. The preliminary observations show that such films are elastic solids of high compressibility, very much like protein films on water. With stearic acid, films at a water-air and an oil-water interface are very different, usually being condensed in the first case and gaseous in the second.

[4] I. Langmuir, *Jour. Chem. Phys.*, 1: 756, 1933.

Most of the experiments described in this paper have been carried out with egg-albumin on distilled water brought to about pH 7 by the addition of a trace of ammonia. In some cases we have changed the pH to 3 and to 10 but have not observed any marked differences in behavior. A few experiments with pepsin and insulin have shown similar behavior. Undoubtedly by the application of these methods, quantitative differences will be found between the proteins which form monolayers on water.

The addition of formaldehyde to the water under a protein film has been found to decrease greatly the compressibility of these films, presumably by forming new cross-linkages which prevent the waviness of the lower surface or hold the waves more nearly rigid.

The properties of proteins shown by our experiments seem to be in accord with the view that the protein monolayer is a two-dimensional network held together by strong elastic springs and are not in accord with a structure consisting of polypeptide chains.

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