CONSTRUCTION OF A SURFACE PRESSURE BALANCE
AND THE MEASUREMENT OF THE AREA OF A
MOLECULE OF XANTHOPHYLL

by

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## INTRODUCTION

Due to the manner in which the molecules are arranged,
the study of films provides a simple method of investigating
the properties of molecules. The films are of one molecule
in thickness, and the molecules in them assume a definite
orientation relative to the surface. The experimental meth-
od enables forces tangential to the surface to be measured,
and direct information is obtainable as to some of the
forces between the molecules composing the film. By study-
ing different compounds the effect of chemical constitution
upon the properties of these films can be noted, from which
information concerning the structure and dimensions of the
molecules can be gained.

The absorption of food into the blood stream and its
assimilation in the body are definitely connected with sur-
face phenomena. The behavior of any compound at a surface
is determined to a great extent by the structure of its
molecules, especially by the presence of polar groups and
their relation to the remainder of the molecule.

The function of carotenoids in animals has been the
subject of considerable investigation in recent years. It
is the purpose of the present study to investigate the

molecular structure of xanthophyll by determining its molec-
ular area and the orientation of the molecules in an aqueous
surface.

## HISTORICAL

Pockels (14) studied the damping effect of films on
waves. She found that surface films could be handled by
pushing them in front of strips or "barriers" extending the
whole width of a trough of water filled to the brim. By
sliding these barriers along the tray the area of water on
which a given quantity of oil could spread was varied at
will.

Pockels showed that very small amounts of oil on the
surface of water in the trough had no appreciable effect on
the surface tension, but that the surface tension began to
decrease suddenly when the amount of oil per unit area was
increased beyond a certain definite limit.

Raleigh (15) repeated these experiments and clearly
pointed out the importance of the phenomena in the explana-
tion of surface tension. He measured the surface tension
of the contaminated water between the barriers by the Wil-
helmy method; i. e., a thin blade was mounted in a balance,
its plane vertical, and the lower horizontal edge dipping
under the surface of the water. As the thickness of the oil

film was varied by shifting the position of one of the barriers, the surface tension changed. Raleigh investigated castor oil and olive oil, and found that castor oil begins to have an appreciable effect on the surface tension of water when it is present in sufficient quantity to form a layer $1.3 \times 10^{-7}$ cm. thick. When the thickness is increased beyond this point the surface tension falls rapidly and finally reaches a point where there is only slight further decrease. With olive oil Raleigh found the thickness at which the tension begins to fall is $1.0 \times 10^{-7}$ cm. He suggested that, at this critical point, the molecules are just crowded together into a layer one molecule thick, touching each other over the whole surface.

Devaux (7) extended this work and developed experimental methods for the study of oil films which demonstrated the presence of monomolecular oil films. He determined the areas covered by monomolecular films from weighed amounts of oils. Knowing the volume of oil added and the area covered by it, he could calculate the thickness of the film. Devaux considered that this thickness represented the diameter of a molecule, and it agreed well with the value calculated from a consideration of the molecular weight and density of the oil, and Avogadro's number. He found that the film of triolein was $1.1 \times 10^{-7}$ cm. thick as compared with the theoret-

ical value of $1.13 \times 10^{-7}$ cm. This agreement furnished conclusive proof that the molecules are in a monomolecular layer.

Langmuir (13) introduced new experimental methods into the study of these films. Adam and Jessop (4) and Freud (8) have modified Langmuir's apparatus and technique.

## THEORETICAL

### Surface Tension

The fact that a liquid surface contracts spontaneously indicates that there is free energy associated with it and that work must be expended to extend the surface. This work is done in bringing molecules from the interior of the liquid to the surface against the inward attractive forces. This work or free energy of the surface will be a definite amount since there will always be a definite number of molecules in the surface. The free energy of the surface is usually replaced by a hypothetical tension, known as the surface tension, acting in all directions parallel to the surface. The surface tension has the same dimensions as the free surface energy and it has the same numerical magnitude.

## Spreading of Liquids

When a drop of a liquid is placed on the surface either of another immiscible liquid, or of a solid, it may spread to a film, or remain as a drop without spreading. The surface tensions of the two liquids, and the interfacial tension between them, determine whether or not the liquid spreads; and the same holds if the lower phase is a solid.

If a drop of liquid B is placed on liquid A, the surface of A disappears and the surface of B and the interface AB appear. The accompanying free energy decrease is

$$S = r_A - (r_B + r_{AB}) \tag{1}$$

where symbol $r$ denotes the surface tension or surface free energy.

The work of adhesion necessary to pull apart the one sq. cm. of interface AB is given by the equation of Dupre as

$$W_{AB} = r_A + r_B - r_{AB} \tag{2}$$

The work of cohesion or the work required to break a column of liquid B one sq. cm. in cross-section is

$$W_B = 2 r_B \tag{3}$$

Combination of (1), (2) and (3) gives

$$S = W_{AB} - W_B \tag{4}$$

which indicates that spreading occurs if work of adhesion is greater than cohesion work of the spreading liquid.

Harkins has called S the spreading coefficient of B on A. The essential condition for spreading is simply that the upper liquid must adhere to the lower more strongly than it adheres to itself. (6)

## Molecular Orientation in Surfaces

Langmuir (12,13) and Harkins (9) have independently developed the theory of surface tension in which the orientation of the molecules in the surface is regarded as the principal factor in determining the surface tension. The basis of the theory is that certain molecules contain polar groups which are characterized by a strong stray field or residual valence. These stray fields are due to the non-symmetrical arrangement of the electrons of the atoms constituting the active portion of the molecule, and give rise to electric or dipole moments. Molecules such as those of NaCl and such groups as the -OH, -COOH, and -C$_\zeta^{O}$ have high electric moments, while molecules such as $CH_4$, $C_6H_6$, or the corresponding alkyl groups have low electric moments and consequently weak stray fields or residual valences.

If a molecule consisting of a non-polar alkyl group and a polar group attached to one end were introduced into

the surface of a polar liquid, the molecule would be expected to orient itself with the polar group toward the bulk of the liquid and the non-polar end outwards toward the surrounding phase. Evidence that such orientation occurs is to be found in a comparison of the surface tensions of the liquid hydrocarbons of the paraffin series with the surface tension of the corresponding alcohols. It is found that the tensions of all members of both series are practically identical, indicating that the non-polar methyl groups at the ends of the hydrocarbon chains form the surface layer in both cases, the polar hydroxyl group being drawn into the liquid and having little effect on the surface tension.

Evidence is also gained by comparing the work of cohesion, or twice the surface tension, of compounds of related constitution with their work of adhesion to water. The cohesional work is a measure of the intensity of the attraction between two free surfaces of the same liquid about to come in contact. It is found that the cohesional work varies much less than the adhesional work to water; that is, the attraction of the free surface of a liquid such as an alcohol or acid of medium length chain for a similar surface is but little greater than the attraction of one purely paraffin surface for another. Two -OH or -COOH groups in contact

would attract each other strongly; therefore it is concluded
that these groups are buried beneath the hydrocarbon groups
at the surface.

Further evidence of molecular orientation in surfaces
is derived from experiments on thin films of insoluble sub-
stances on water, which will be discussed.

## Surface Films of Insoluble Substances

As indicated in a preceding section, if an insoluble
substance whose molecules possess a greater attraction for
water than for the substance itself is placed on a clean
surface of water, it will spread out into a surface film.
The film may be expected to be one molecule in thickness,
since the affinities of the molecules will be better satis-
fied if every one is in contact with the water.

When the film is subjected to lateral compression, the
first point at which the surface tension of the water is re-
duced is reached when the molecules form a single layer in
contact, and the lateral compression on the film is equal to
the diminution of the surface tension of the water.  The
latter statement is verified by a consideration of the work
done by a small displacement dx of the float separating a
region of surface covered by a film from a clean surface.
If the film exerts a pressure of F dynes per cm. on the

float, then the displacement dx does an amount of work Fldx
where l is the length of the float. But the work done in
replacing an area ldx, of water of surface tension or sur-
face free energy   , by a film-covered surface of surface
tension $\gamma$ , is also ($\gamma - \gamma'$)ldx. Hence, Fldx = ($\gamma - \gamma'$)ldx
or $F = \gamma - \gamma'$.

Types of Films. Adam and coworkers (1, 2, 3, 4, 5)
have shown that there are four types of surface films formed
depending upon the amount of lateral adhesion between the
film molecules. They are:

1. Gaseous films

2. Condensed films

3. Liquid expanded films

4. Vapor expanded films.

The ideal gaseous film would consist of molecules of
negligible size, insoluble in water, and without any lateral
adhesion for one another, though with sufficient adhesion
for the water to prevent their flying off as a vapor. The
ideal gaseous film is unrealizable experimentally, but its
properties are of value for comparison with actual gaseous
films. The actual films are distinguished by the fact that
they exert a pressure at very great areas per molecules, and
they follow the perfect two dimensional gas law fairly close-
ly, the deviations from the law being analagous to the

deviations of gases from the perfect gas law.

The perfect gas law or the two dimensional equation of state is

$$FA = RT \tag{5}$$

where $F$ is the surface pressure in dynes per cm.; $A$ is the area per molecule in sq. cm.; $R$ is the gas constant, $1.372 \times 10^{-16}$ ergs per molecule; and $T$ is the absolute temperature.

The theoretical basis of equation (5) involves the following essentials. For the equilibrium between a solute 2 in a solvent 1 and a surface film, Gibbs's adsorption law governs:

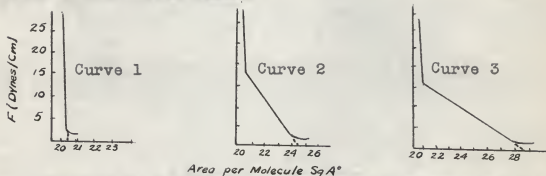$$1/a = \Gamma_2 = \frac{dF}{d\mu_2} = \frac{dF}{RT \, d \ln a_2} \tag{6}$$

in which $\Gamma$ is the adsorption in molecules per cm.$^2$, $R$ is $1.372 \times 10^{-16}$, $\mu_2$ and $a_2$ are the potential and activity of the solute.

Applying Langmuir's kinetic theory of adsorption, when the concentrations and adsorptions are small, the rate of condensation of molecules from the interior of the solution on the vacant places in the film is proportional to the concentration and activity in the solution, the vacant spaces being practically equal to the whole area of the surface. The rate of condensation is proportional to $a_2$. In the dilute adsorbed film the molecules do not affect each other

appreciably; therefore the average time of life of each
molecule in the film is independent of the number present,
and the rate at which the molecules leave the film for the
interior is proportional to the number present, that is, to
$\Gamma_2$. The rate of condensation on the film is equal to the
rate of leaving the film; $\Gamma_2$ or $1/a$ is proportional to $a_2$.
Combining with equation (6) we obtain $FA = RT$.

To extend this reasoning to insoluble films, we make
the assumption usually considered justifiable by statistical
mechanics, that the immeasurably small concentrations and
activity have a definite numerical value.

The condensed film is formed by substances whose mole-
cules have a great deal of lateral adhesion. The molecules
form compact clumps which they seldom leave to travel over
the surface. There are two kinds of condensed films as
shown in the curves below.



Area per Molecule Sq A°

Curve 1 is for fatty acids on distilled water; it is
typical of the "close-packed chain" class of condensed film,
and is also given by the dibasic esters, amides, and methyl

ketones.

Curve 2 is given by the saturated acids on dilute hydrochloric acid; curve 3 is given by unsaturated iso-oleic acid. These curves are typical of the class of condensed film known as "close-packed heads, rearranged by compression."

Curve 2 extrapolated to zero pressure cuts the abscissa at 25 sq. Å per molecule, while curve 3 cuts it at 28.7 sq. Å. It is thus evident that the areas are dependent upon the end group of the molecule, the CH:CHCOOH group of iso-oleic acid being larger than the COOH group of the saturated acids. Since the molecules are apparently in close contact in both cases, the difference in area must be due to differences in the packing of the molecules caused by the variations in the shape of and forces around the molecules.

The liquid expanded film is characterized by properties intermediate between those of gaseous and condensed films. Compounds which form condensed films at low temperatures usually form liquid expanded films at higher temperatures. The fatty acids, nitriles, alcohols, amides, ureas, oximes and acetamides undergo this transition with temperature. The distinguishing characteristic of these films is that they tend to reach a definite limiting area at zero compression, and have a constant surface vapor pressure.

The vapor expanded film is similar to the liquid expanded film, but differs in that there is no definite limiting area or surface vapor pressure.

Condensation Phenomena. At large area and below a certain temperature, which is analogous in two dimensions to the critical temperatures of liquids in three dimensions, condensed films of the fatty acids exhibit a region of constant surface pressure. Upon further increase of the area, the pressure falls and the curve follows the equation of the ideal gaseous film fairly closely. The region of constant pressure corresponds to the vapor pressure of liquids, and it indicates the presence of an equilibrium between the two surface phases, the vapor film and the islands of liquid film in which the molecules are adhering.

## EXPERIMENTAL

### Apparatus

The instrument used in this investigation is pictured in Plate I. The microbalance is mounted in a rigid brass frame, designed to fit a carefully machined brass trough. The trough is 60 cm. long, 15 cm. wide, and 1.8 cm. deep. The float consists of a strip of copper 11.60 cm. long, connected to the frame by strips of platinum ribbon 0.003 mm. in thickness and 5 mm. wide. In order to adjust the height

Plate I.  The surface pressure balance.

Plate I

of the ribbons to varying levels of the film, they are soldered to end plates, to which are attached screws whose motion raises or lowers the ribbons.

The force exerted by the film on the float is transmitted to the torsion wire by means of the triangular framework. Two prongs of this framework enter holes in the float. The framework is attached to the torsion wire by a clamp similar to that found on the Du Nouy tensiometer. The upper plate also carries the counterbalance for the regulation of the center of gravity. This arrangement proved to be more satisfactory than soldering the triangle to the torsion wire, since it avoids heating the torsion wire and provides a convenient method of changing or replacing the torsion wire.

The horizontal arms of the balance are provided with sharp triangular notches at a distance of 7.22 cm. from the torsion wire. Small weights are supported in these notches when the torsion wire is calibrated. The vertical arm of the balance is 10.10 cm. in length.

One end of the torsion wire is held in a clamp attached to a graduated circle, equipped with a vernier. The other end of the torsion wire is held in a clamp arrangement which serves to adjust the tension. A No. 32 B & S gauge phosphor-bronze torsion wire is used for all pressures above 0.5 dynes per cm. For accurate measurement of low pressures a

No. 36 or 40 B & S gauge phosphorbronze wire is used.

The position of the float is marked by an optical lever. The image of a scale fixed to the rear wall of the cage in which the instrument is enclosed is reflected from a mirror mounted in an adjustable stand at the front of the cage. This image is then reflected by a small mirror attached to the vertical arm of the triangle of the microbalance, and this second reflection is viewed in a telescope focused on the image in the small mirror. Thus, small movements of the float are highly magnified. Rotation of the graduated circle is controlled by a micrometer dial which has a gear ratio of 10:1.

The area of the film is regulated by means of paraffined plate glass barriers, which are moved by the stirrups of a carrier.

The instrument is enclosed in a rectangular sheet metal box, shown in Plate II, in order to keep any dust from reaching the surface of the trough, and to provide a means of working in an atmosphere of inert gas. The barrier carriers and the micrometer dial controlling the rotation of the graduated circle are operated from the outside of the cage.

Temperature control is effected by partial immersion of the instrument in a water bath through which tap water is constantly circulated.

Plate II.  Cage for surface pressure balance for
operation in an atmosphere of nitrogen.

Plate II

A known amount of material is delivered on the surface
by means of a special weight pipette. Caps which fit tight-
ly over the ends of the pipette minimize evaporation of the
solvent.

## Manipulation

The method of cleaning the trough consists of rubbing
it with emery paper under a stream of tap water until it is
wetted by the water. It is then rinsed with boiling conduc-
tivity water and allowed to dry. A ten per cent solution of
paraffin in benzene is painted on the trough while it is
still hot.

The microbalance is cleaned by immersing it in toluene
contained in a small tray. The float, the upper half of the
platinum ribbons, and the end plates are paraffined with the
dilute solution of paraffin in benzene.

The trough is filled with 1800 cc. of conductivity
water and the surface cleaned by sweeping with the glass
barriers. Any contamination is removed by means of suction.
The water removed with suction is caught in a trap, and an
equal amount is returned to the trough.

A zero reading of the telescope scale and vernier is
taken. The torsion wire is calibrated by placing 10, 50,
and 500 mg. weights in the notches on the horizontal lever

arm. The telescope scale is brought back to the zero reading by rotation of the graduated circle. The force in dynes per cm. on the float corresponding to one degree of rotation is calculated by means of the equation

Dynes/cm. = $\dfrac{\text{Weight (mg.) x 0.9806 x Horizontal lever arm}}{\text{Vertical lever arm x effective length of float}}$

The effective length of the float is equal to the length of the float plus one-half the length of the gap filled by the platinum foil. The distance between the endplates is 14.29 cm., the length of the float 11.60 cm. Hence, the effective length of the float is

$$11.60 + \frac{14.29 - 11.60}{2} = 12.944 \text{ cm.}$$

The vertical lever arm is 10.10 cm., the horizontal arm, 7.22 cm. in length.

Forces up to 0.5 dynes per cm. on the float are measured by observing the deflections of the telescope directly. The value of one mm. deflection of the scale is found by placing a 10 mg. weight on the horizontal arm and then noting the deflection.

A 0.05 per cent solution of the compound being investigated is prepared, and from 0.1 to 0.2 grams are introduced on the surface by use of the weight pipette. The solvent used must be volatile and insoluble in water, and may be benzene, petroleum ether, or chloroform, depending on the solubility of the compound.

## Calculations

The Force Area curves are determined by plotting the force F in dynes per cm. on the float against the corresponding area per molecule.

F is calculated by multiplying the degrees of rotation of the graduated circle by the equivalent of one degree in dynes per cm. on the float. The latter quantity was determined in the calibration of the torsion wire.

The area per molecule is calculated from a consideration of the weight of solution delivered on the surface. A known amount of substance is dissolved in a given weight of solvent. Then,

$$\frac{\text{Weight of solute} \times 6.06 \times 10^{23}}{\text{Molecular weight solute} \times \text{Weight of solution}} = \text{Molecules/gr. of solution}$$

and,

$$\frac{\text{Molecules/gr. of solution} \times \text{Grams delivered} \times 10^6}{\text{Area of surface covered (cm.}^2)} = \text{Area/molecule (Sq. Å)}$$

## DISCUSSION OF RESULTS

The cross-sectional area of stearic acid was determined on various substrates. Table 1 shows the result of such a determination on .01 N. HCl. Distilled water five days old was used to make up the solution.
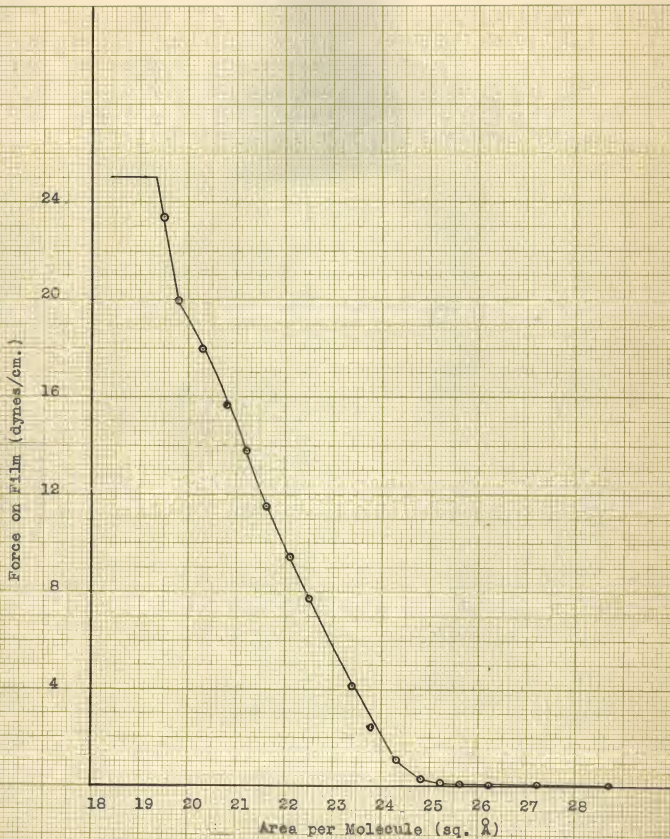
Table 1.  F A Determination of Stearic Acid.

Substrate:  0.01 N. HCl
Zero of Telescope Scale:  70.00,
Zero of Vernier          46°50'
Gr. Solution Delivered   0.2663
Molecules Delivered      16.05 x 10^16
Temperature              25° C.

| Scale Reading on Trough | Length of Film (cm.) | Area of Film (cm.²) | Area per Molecule | Vernier Reading | Degrees Rotation | Dynes per cm. on Float |
|---|---|---|---|---|---|---|
| 50.0 | 36.5 | 547 | 34.1 Å | 46°50' | 0 00 | |
| 43.5 | 29.8 | 446 | 27.8 | 47 00 | 0 10' | 0.017 |
| 42.5 | 29.0 | 435 | 27.2 | 47 06 | 0 16 | 0.045 |
| 41.5 | 28.0 | 419 | 26.2 | 47 15 | 0 25 | 0.071 |
| 41.0 | 27.5 | 412 | 25.6 | 47 20 | 0 30 | 0.085 |
| 40.5 | 27.0 | 404 | 25.2 | 47 45 | 0 55 | 0.154 |
| 40.0 | 26.5 | 397 | 24.8 | 48 40 | 1 50 | 0.310 |
| 39.5 | 26.0 | 389 | 24.3 | 52 50 | 6 00 | 1.102 |
| 39.0 | 25.5 | 382 | 23.8 | 61 12 | 14 22 | 2.44 |
| 38.5 | 25.0 | 375 | 23.4 | 71 25 | 24 35 | 4.16 |
| 38.0 | 24.5 | 368 | 23.0 | 61 15 | 34 25 | 7.00 |
| 37.5 | 24.0 | 361 | 22.5 | 87 35 | 45 35 | 7.75 |
| 37.0 | 23.5 | 354 | 22.1 | 77 35 | 55 35 | 9.42 |
| 36.5 | 23.0 | 347 | 21.6 | 65 00 | 68 10 | 11.02 |
| 36.0 | 22.5 | 340 | 21.2 | 52 00 | 81 10 | 13.75 |
| 35.5 | 22.0 | 333 | 20.8 | 40 30 | 92 40 | 15.72 |
| 35.0 | 21.5 | 326 | 20.3 | 27 35 | 105 35 | 17.95 |
| 34.5 | 21.0 | 319 | 19.8 | 15 00 | 118 10 | 20.00 |
| 34.0 | 20.5 | 312 | 19.5 | 5 00 | 138 02 | 23.40 |
| 33.5 | 20.0 | 305 | 19.1 | 15 20 | 148 05 | 25.00 |

Film collapsed

Table 2 is the data obtained when the substrate was dis-
tilled water one month old, to which was added sufficient
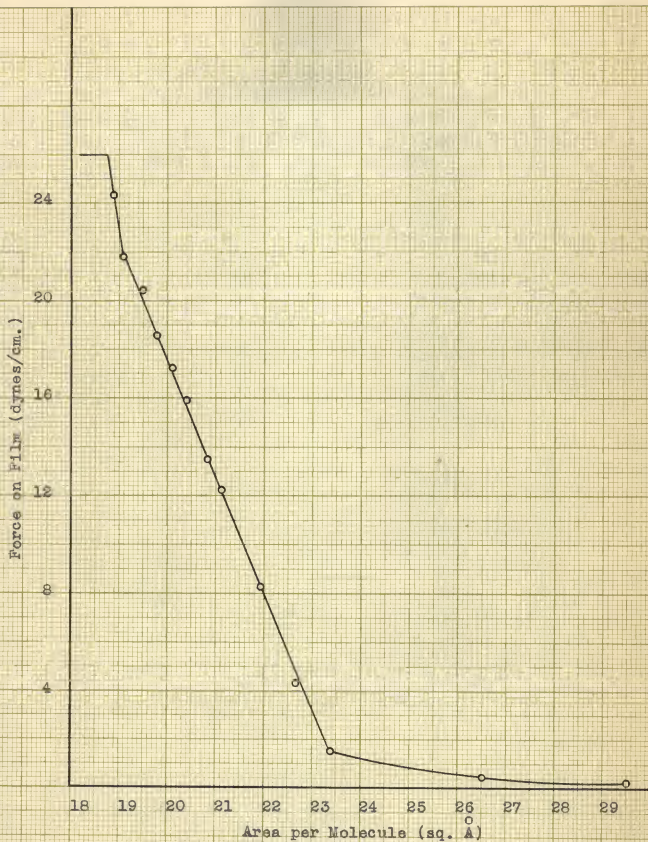HCl to make a .005 N. solution.

Fig. 1.  F A Determination of Stearic Acid on 0.01 N. HCl

Table 2.  F A Determination of Stearic Acid.

Substrate:  .005 N. HCl
Zero of Telescope Scale:  70.00
Zero of Vernier  2°00' L
Gr. Solution Delivered  0.2603
Molecules Delivered  9.83 x $10^{16}$
Temperature  23.5° C.

| Scale Reading on Trough | Length of Film (cm.) | Area of Film (cm.²) | Area per Molecule | Vernier Reading | Degrees Rotation | Dynes per cm. on Float |
|---|---|---|---|---|---|---|
| 50.0 | 37.4 | 561 | 67.1 Å | 1.0 mm. | | 0.054 |
| 48.0 | 35.4 | 531 | 54.0 | 2.0 | | 0.108 |
| 46.0 | 33.4 | 501 | 50.9 | 4.0 | | 0.216 |
| 44.0 | 31.4 | 471 | 47.9 | 4.5 | | 0.242 |
| 42.0 | 29.4 | 441 | 44.8 | 4.5 | | 0.242 |
| 40.0 | 27.4 | 411 | 41.8 | 5.0 | | 0.269 |
| 38.0 | 25.4 | 381 | 38.8 | 5.0 | | 0.269 |
| 36.0 | 23.4 | 351 | 36.7 | 5.5 | | 0.296 |
| 34.0 | 21.4 | 321 | 32.6 | 6.0 | | 0.324 |
| 32.0 | 19.4 | 291 | 29.6 | 6.5 | | 0.330 |
| 30.0 | 17.4 | 261 | 26.6 | 8.0 | | 0.432 |
| 28.0 | 15.4 | 231 | 23.5 | 7°30' | 9°30' | 1.55 |
| 27.5 | 14.9 | 223 | 22.8 | 24°45' | 26 45 | 4.38 |
| 27.0 | 14.4 | 216 | 22.0 | 48 20 | 50 20 | 8.25 |
| 26.7 | 14.1 | 211 | 21.5 | 64 15 | 66 15 | 11.85 |
| 26.5 | 13.9 | 209 | 21.2 | 72 30 | 74 30 | 12.20 |
| 26.3 | 13.7 | 205 | 20.9 | 80 05 | 82 05 | 13.45 |
| 26.0 | 13.4 | 201 | 20.5 | 94 30 | 96 30 | 15.95 |
| 25.8 | 13.2 | 198 | 20.2 | 103 00 | 105 00 | 17.21 |
| 25.6 | 13.0 | 195 | 19.9 | 113 00 | 115 00 | 18.55 |
| 25.4 | 12.8 | 192 | 19.6 | 122 15 | 124 15 | 20.40 |
| 25.2 | 12.6 | 189 | 19.2 | 129 45 | 131 45 | 21.60 |
| 25.0 | 12.4 | 186 | 19.0 | 146 00 | 148 00 | 24.30 |

The data of Tables 1 and 2 are plotted in Figures 1 and 2.

Fig. 2. F A Determination of Stearic Acid on .005 N. HCl

It will be noted that the curves consist of two portions which differ in slope. The extrapolation of the lower part of the curve to zero compression gives an area which is a measure of the polar group of the molecule. The curve in Figure 1 gives an area of 24.4 sq. Å; that in Figure 2 gives an area of 24.5 sq. Å. These values agree fairly well with the value of 25 sq. Å given by Adam (3). Since, however, we do not know the orientation of the end groups to the surface, this area does not give direct information as to the real size of the group.

The upper portion of the curves when produced cut the abscissa at 21.6 sq. Å, which is in fairly close agreement with Adam's value of 20.5 sq. Å, in consideration of the fact that the curves were obtained at a slightly higher temperature. This portion of the curve corresponds to the condition in which the long chains of the molecules are closely packed and nearly vertical. X-ray measurements on fatty acids have shown that the cross section perpendicular to the chain is 18.4 sq. Å in area. Either, then, the molecules are less closely packed than in crystals or they are tilted in the film.

All of the films investigated showed hysteresis or elastic after working. Upon decreasing the area the pressure rose and then fell to an equilibrium value. When the area

was increased the pressure fell and then rose to an equilibrium value. The time required was dependent upon the pressure on the film, and on the substrate. The time lag decreased as the acidity of the substrate was increased. Table 3 shows the instantaneous and equilibrium values on the compression curve of stearic acid on 0.01 N. HCl. These instantaneous and equilibrium values are plotted as curves 1 and 2 respectively in Figure 3. Table 4 shows the variation of the pressure with time at various areas in the data of Table 3. These data are plotted in Figure 4.

Adam (2, 3) has noted hysteresis in the films of myristic acid, hydrolecithin, and dodecyl phenol. In the case of myristic acid only one-half minute is required to obtain equilibrium values, while in the case of hydrolecithin and of dodecyl phenol ten minutes are required. Adam apparently did not note any hysteresis in the films of stearic acid. However, Harkins and Fischer (10) find marked hysteresis in the decompression curve of stearic acid, both as to pressure and as to surface potential. It was noted that those films which showed the maximum elastic afterworking also exhibited greater area per molecule. It is evident that the molecules require an appreciable length of time to reach a stable configuration.

Table 3. Hysteresis in Stearic Acid Films.

Substrate: 0.01 N. HCl
Zero of Telescope Scale: 70.00
Zero of Vernier 2°00' L.
Gr. Solution Delivered 0.1010
Molecules Delivered 10.18 x 10^16
Temperature 24° C.

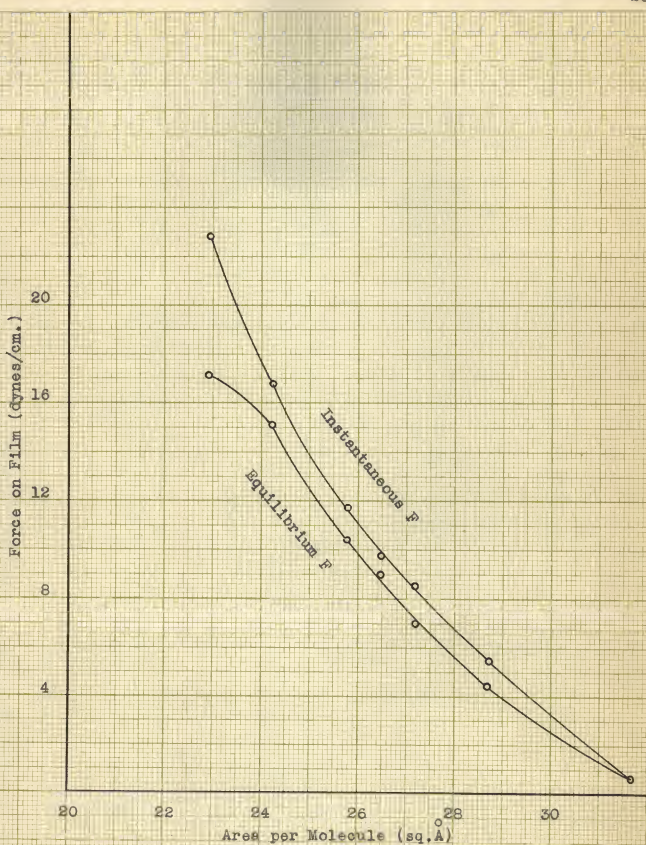| Scale Reading on Trough (cm.) | Length of Film (cm.) | Area of Film (cm.²) | Area per Mole-cule | Vernier Equil. Reading | Degrees Rota-tion | Dynes per cm. on Float | Vernier Inst. Reading | Degrees Rota-tion | Dynes per cm. on Float |
|---|---|---|---|---|---|---|---|---|---|
| 34.0 | 20.5 | 308 | 31.7 | 3°00' R | 5°00' R | 0.492 | 3°00' | 5°00' | 0.492 |
| 32.0 | 19.5 | 293 | 28.8 | 26 00 | 28 00 | 4.58 | 32 40 | 34 40 | 5.68 |
| 31.0 | 18.5 | 278 | 27.3 | 42 00 | 44 00 | 7.21 | 50 45 | 52 45 | 8.65 |
| 30.5 | 18.0 | 270 | 26.5 | 53 40 | 55 40 | 9.14 | 58 05 | 60 05 | 9.85 |
| 30.0 | 17.5 | 262 | 25.8 | 62 25 | 64 25 | 10.55 | 71 00 | 73 00 | 11.95 |
| 29.0 | 16.5 | 258 | 24.4 | 91 05 | 93 05 | 15.25 | 100 42 | 102 42 | 16.88 |
| 28.0 | 15.5 | 233 | 22.9 | 105 55 | 105 55 | 17.20 | 137 35 | 139 35 | 22.90 |

Fig. 3. Hysteresis in Film of Stearic Acid on .01 N. HCl

Table 4.  Variation of Pressure with Time in Stearic Acid Film.

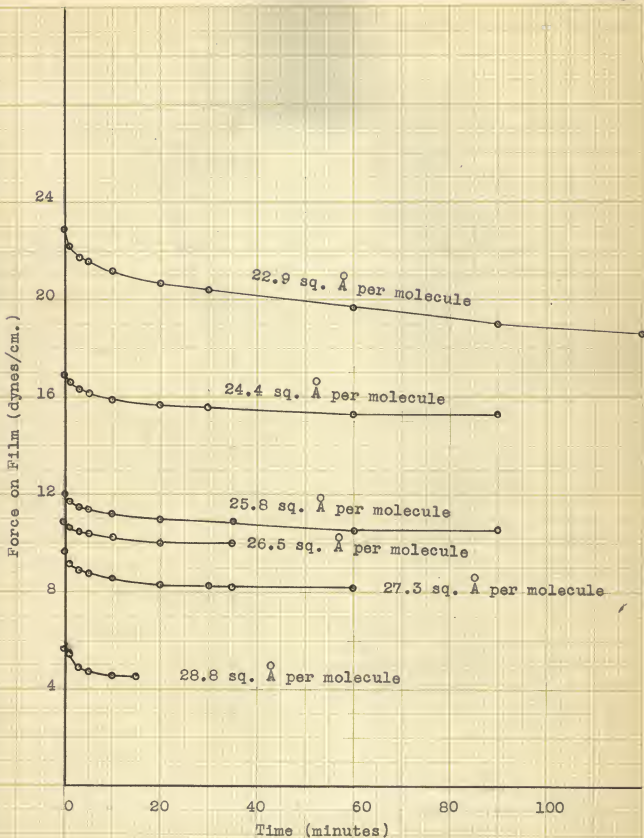| Time | 28.8 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. | 27.3 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. | 26.5 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. | 25.8 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. | 24.4 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. | 23.3 A²/mol. Deg. Rota-tion on Fl. | Dynes per cm. on Fl. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 min. | 34°40' | 5.69 | 52°45' | 8.65 | 60°05' | 9.86 | 73°00' | 12.0 | 108°42' | 16.9 | 13?°35' | 22.9 |
| 1 | 32 25 | 5.32 | 50 00 | 8.20 | 58 57 | 9.65 | 71 29 | 11.7 | 101 02 | 16.6 | 135 35 | 22.2 |
| 3 | 30 10 | 4.04 | 48 06 | 7.88 | 57 55 | 9.50 | 70 28 | 11.5 | 99 41 | 16.3 | 135 00 | 21.8 |
| 5 | 29 00 | 4.75 | 47 28 | 7.78 | 57 12 | 9.38 | 69 34 | 11.4 | 99 40 | 16.2 | 131 58 | 21.6 |
| 10 | 28 00 | 4.60 | 46 22 | 7.60 | 56 18 | 9.23 | 68 30 | 11.2 | 97 10 | 16.9 | 129 12 | 21.2 |
| 20 | 28 00 | 4.60 | 44 25 | 7.28 | 53 41 | 8.98 | 67 33 | 11.0 | 95 28 | 15.7 | 126 25 | 20.7 |
| 30 | | | 44 06 | 7.23 | 55 41 | 8.98 | 66 20 | 11.9 | 94 40 | 15.6 | 124 20 | 20.4 |
| 35 | | | 44 00 | 7.21 | | | | | | | 121 50 | 20.0 |
| 60 | | | 44 00 | 7.21 | 55 41 | 8.98 | 64 18 | 10.5 | 93 05 | 15.3 | 120 00 | 19.7 |
| 90 | | | | | | | 63 57 | 10.5 | 93 05 | 15.3 | 115 50 | 19.0 |
| 120 | | | | | | | 64 25 | 10.8 | | | 113 28 | 18.6 |
| 135 | | | | | | | | | | | | |
| 185 | | | | | | | | | | | 109 30 | 18.0 |
| 210 | | | | | | | | | | | 109 00 | 17.9 |
| 600 | | | | | | | | | | | 105 00 | 17.2 |

Fig. 4. Variation of Force with Time in Film of Stearic Acid

## Table 5.  F A Determination of Xanthophyll.

Substrate:  0.01 N. HCl + 0.12% Hydroquinone
Zero of Telescope Scale:  70.00
Zero of Vernier  26°35' R
Grams Solution Delivered  0.1879
Molecules Delivered  2.52 x 10$^{16}$
Temperature  24° C.

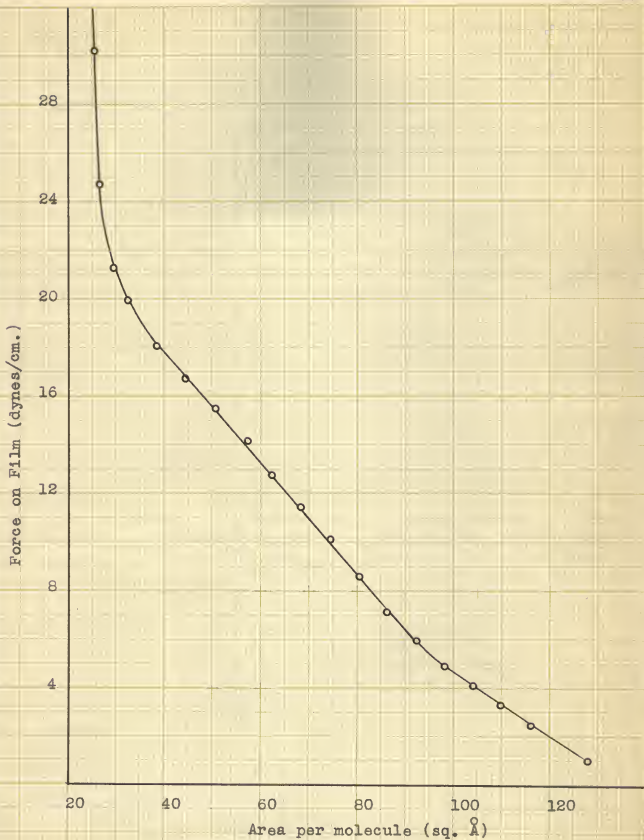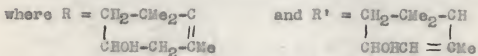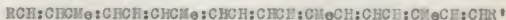| Scale Reading on Trough | Length of Film (cm.) | Area of Film (cm.²) | Area per Molecule | Vernier Reading | Degrees Rotation | Dynes per cm. on Float |
|---|---|---|---|---|---|---|
| 50.0 | 37.5 | 563 | 223.0 Å | 2.0 mm. | | 0.108 |
| 48. | 35.5 | 533 | 211.5 | 2.5 | | 0.135 |
| 46. | 33.5 | 503 | 199.5 | 3.0 | | 0.162 |
| 44. | 31.5 | 473 | 187.5 | 3.0 | | 0.162 |
| 42 | 29.5 | 443 | 175.5 | 3.5 | | 0.189 |
| 40 | 27.5 | 413 | 164.0 | 4.5 | | 0.242 |
| 38 | 25.5 | 383 | 152.0 | 6.0 | | 0.324 |
| 36 | 23.5 | 353 | 140.0 | 10.0 | | 0.540 |
| 34 | 21.5 | 323 | 127.8 | 32°50' R | 6°15' | 1.03 |
| 32 | 19.5 | 293 | 116.0 | 41 50 | 15 15 | 2.50 |
| 31 | 18.5 | 278 | 109.9 | 46 58 | 20 23 | 3.32 |
| 30 | 17.5 | 263 | 104.0 | 51 37 | 25 02 | 4.10 |
| 29 | 16.5 | 248 | 98.1 | 56 45 | 30 10 | 4.93 |
| 28 | 15.5 | 233 | 92.2 | 63 4 | 36 29 | 5.97 |
| 27 | 14.5 | 218 | 86.2 | 70 15 | 43 40 | 7.11 |
| 26 | 13.5 | 203 | 80.5 | 79 07 | 52 32 | 8.60 |
| 25 | 12.5 | 188 | 74.3 | 88 41 | 62 06 | 10.2 |
| 24 | 11.5 | 173 | 68.4 | 96 33 | 69 58 | 11.5 |
| 23 | 10.5 | 158 | 62.4 | 104 50 | 78 15 | 12.8 |
| 22 | 9.5 | 133 | 57.5 | 113 15 | 86 40 | 14.2 |
| 21 | 8.5 | 118 | 50.5 | 121 35 | 95 00 | 15.6 |
| 20 | 7.5 | 103 | 44.5 | 129 20 | 102 45 | 16.8 |
| 19 | 6.5 | 88 | 38.6 | 137 00 | 110 25 | 18.1 |
| 18 | 5.5 | 73 | 32.7 | 148 15 | 121 40 | 20.0 |
| 17.5 | 5.0 | 75 | 29.7 | 156 30 | 129 55 | 21.3 |
| 17.0 | 4.5 | 67.5 | 26.7 | 144 25 | 144 25 | 24.7 |
| 16.8 | 4.3 | 64.6 | 25.6 | 184 25 | 184 25 | 30.2 |
| 16.3 | 3.8 | | 22.0 | 289 00 | 289 00 | 47.5 |

Fig. 5. F A Determination of Xanthophyll on 0.01 N. HCl

Table 5 is the result of a Force-Area determination (re-checked) of xanthophyll. The substrate in this case was 0.01 N. HCl with 0.12 per cent hydroquinone. Hughes and Rideal (11) thought that this contration of hydroquinone was sufficient to inhibit the atmospheric oxidation of $\alpha$ and $\beta$ elaeostearic acids. The determination was carried out in an atmosphere of nitrogen as a further precaution to prevent oxidation of the film. Xanthophyll also exhibited hysteresis.

The data in Table 5 are plotted in Figure 5. The curve consists of two portions which differ in slope. The lower portion of the curve extrapolates to an area of 118 sq. $\overset{\circ}{A}$ per molecule at no compression. In this portion of the curve the film is in the expanded state, the molecules lying flat on the surface. This orientation could be expected from a consideration of the structure of the xanthophyll molecule:

$$RCH:CHCMe:CHCH:CHCMe:CHCH:CHCH:CMeCH:CHCH:CMeCH:CHR'$$

where $R = CH_2-CMe_2-C$     and $R' = CH_2-CMe_2-CH$

              $CHOH-CH_2-CMe$            $CHOHCH = CMe$

The affinities of the OH groups and the polar double bonds are best satisfied when they are in contact with the water.

The upper portion of the curve has a much steeper slope

which indicates that the molecules are in close contact and
are very incompressible. This portion of the curve gives an
area of 30 sq. $\overset{o}{A}$ at no compression. This area is slightly
greater than the area that would be occupied by one benzene
group, but it is unlikely that the xanthophyll molecule would
orient itself in this manner. It seems more likely that the
chain connecting the two benzene rings would distort and
rise from the surface, and that the OH groups would remain
in contact with the water.

## SUMMARY

The construction of a surface pressure balance was
described. Force-Area determinations on films of stearic
acid were made, and the phenomenon of hysteresis investigat-
ed. The carotenoid pigment, xanthophyll was investigated
and was found to occupy a limiting area of 118 sq. $\overset{o}{A}$ per
molecule.

## CONCLUSIONS

1. The phenomenon of hysteresis is exhibited in films
of the fatty acids. This phenomenon has apparently been un-
noticed by some of the earlier investigators in this field.

2. Xanthophyll forms a monomolecular film on the

surface of aqueous solutions, and tends toward a limiting area of 118 sq. $\overset{\circ}{A}$ per molecule.

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