energy in excess of that necessary for the primary process is used to augment reaction 2. However, reaction 3 is only indirectly influenced by the increase of quantum energy since at room temperature all methyl groups have sufficient thermal energy to react with acetaldehyde.

### Summary

1. A detailed study of the gaseous photolysis products of acetaldehyde has been made over the temperature range −40 to +98°. Over this range considerable variation was found in the ratios of the non-condensable products, hydrogen, methane and carbon monoxide.

2. An investigation of the photolysis products which are condensable at the temperature of solid carbon dioxide showed the presence of diacetyl, glyoxal and formaldehyde. With respect to carbon monoxide as a standard of comparison, the quantities of these compounds produced decreased markedly with increase of the temperature from 25 to 100°. Tests for acetone and methylglyoxal gave negative results.

3. A discussion of results is given in which the viewpoint is taken that the only primary dissociation process of acetaldehyde photolysis is one in which methyl and formyl radicals are formed.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# The State of Monolayers Adsorbed at the Interface Solid–Aqueous Solution

BY FREDERICK M. FOWKES AND WILLIAM D. HARKINS

## 1. Introduction

While the pressure–area (*F–A*) relations of insoluble films on water have received much attention, and while a small amount of information is available concerning films formed by adsorption at the surface of a liquid or at an interface between two liquids, nothing has been known of these relations at the interface between a liquid and a solid. The work described in this paper was begun with the idea of determining at least a part of the equation of state of such interfacial films, and in an endeavor to answer the question as to whether such films are solid, liquid, or gaseous in the ordinary pressure–temperature region. Since no method was known for determining the *F–A* relations of such films the first necessary step was to devise such a method, and this will be described later.

The relations have been determined for films adsorbed upon the surface of a solid from an aqueous solution of the adsorbate. The film forming substances used were *n*-butyl alcohol, *n*-butylamine, *n*-butyric acid, propionic acid, acetic acid, and sodium *n*-butyrate. The films were adsorbed at the interface with cleaved stibnite, cleaved talc, polished graphite, or solidified paraffin wax. It was assumed that the pressure–area relations obtained with the solid paraffin would not be very different from those at the interface between a liquid paraffin and water, and this assumption was found to be justified.

## 2. Theory of the Method for the Determination of the Pressure of a Film at the Interface Solid–Liquid

Figure 1 represents a vertical cross section of a system solid–liquid, taken perpendicular to the plane surface, under investigation of the solid, with the contact angle Θ. In accordance with the general relations at interfaces it may be assumed that the free energy, $\gamma_{SL}$, at the solid–liquid interface is less than that, $\gamma_{SV}$, at the phase boundary solid–vapor. Consider that the point O represents the line of contact, perpendicular to the plane of the diagram, between the liquid phase and the solid. If the surface is lowered in its own plane, so that the line O is displaced 1 cm. with respect to the surface of the solid, then the work done by this displacement, neglecting gravita-

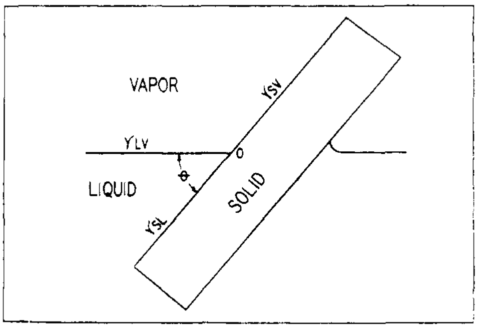

Fig. 1.

tional effects, must be equal to the decrease of free energy. Thus per unit length along O

$$W = \gamma_{SV} - \gamma_{SL} \quad (1)$$

Since $W$ is the amount of work done per unit area of displacement it is justified to assume that $W = tl$, where $l$ is the area, and $t$ is the force per unit length involved in doing the work. Since the force $t$ pulls upward along the surface of the solid it must be balanced by an equal and opposite force, so

$$t = \gamma_{LV} \cos \Theta \quad (2)$$

or

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta \quad (3)$$

Equation 3 holds if the liquid is water (W), or another liquid, or a solution of concentration (C), so

$$\gamma_{SV(W)} = \gamma_{SL(W)} + \gamma_{LV(W)} \cos \Theta_W \quad (4)$$

$$\gamma_{SV(C)} = \gamma_{SL(C)} + \gamma_{LV(C)} \cos \Theta_C \quad (5)$$

It is now possible to calculate the value of

$$F = \gamma_{SL(W)} - \gamma_{SL(C)} \quad (6)$$

for any case in which it can be demonstrated that the value of $\gamma_{SV(C)}$ is sufficiently close to that of $\gamma_{SV(W)}$ to introduce no significant error if the two are assumed to be equal. Obviously this cannot be true with a volatile solute unless the solution is dilute. This question is discussed later from the standpoint of experiment.

For such a case Eqs. 4, 5, and 6 give the relation

$$F = \gamma_{LV(C)} \cos \Theta_C - \gamma_{LV(W)} \cos \Theta_W \quad (7)$$

All of the quantities in this equation, with the exception of $F$, can be determined experimentally, so $F$ can be calculated.

$$F = \gamma_W - \gamma_M \quad (8)$$

Now if the subphase is liquid and the other phase gaseous, $F = \gamma_W - \gamma_M$ is *defined* as the *surface pressure*, and no greater assumption is involved in considering that $F$ acts as a two-dimensional pressure if one of the two phases at the interface is liquid, and the other solid. In Eq. 8 the subscript M indicates a monolayer or film.

The area per molecule in the film is calculated from the film pressures and the activities of the solute by means of the adsorption equation of Gibbs.

**3. Apparatus for the Measurement of Contact Angles.**—Of all the known methods for the determination of contact angle that which uses a tilting plate was chosen as the best for cases in which it can be employed. In order to increase the accuracy of the work an improved apparatus of this type was devised. Perhaps the most important additions were: (1) the use of glass barriers to clean the surface, and (2) the inclusion of a film balance which made it possible either to detect the presence of impurities on a supposedly clean water surface or to determine the surface tension of the solution simultaneously with the measurement of the contact angle.

The main requirements of an accurate instrument for the measurement of contact angles by the tilting plate method are three-fold. First, the surface of the liquid must be kept clean during the period of measurement. This is the condition most often neglected. Second, the observed edge of the solid–liquid intersection must lie on the axis of rotation of the solid surface.[1] Third, there should be a mechanism to move the slide up and down in the liquid, and also in a direction parallel to the length of the slide. The apparatus used in this investigation and shown in Fig. 2 was designed to meet all these requirements. There are two rotational movements consisting of a forty-tooth worm gear and a worm for each unit. There are also two centering devices with rack and pinion movements. The rotating worm (B) turns the slide during a measurement. The corresponding worm gear is fastened to the main shaft, to which the pointer (A) shown in the mirror is also fastened. The main shaft is raised to the proper height by means of the adjustable-height bearing (C). Fastened to the main shaft is the calibrating worm gear box (D), the worm gear of which rotates an inner shaft to which the two mutually perpendicular centering movements are attached. By means of the first centering movement (E) the slide of solid (G) is moved perpendicular to its length, and by the second, (F) parallel to its length. This latter movement dips the slide in and out of the water during measurements. Paraffined glass barriers (H) are used to sweep the surface of the liquid in the paraffined glass trough. A small Wilhelmy type surface tension balance is used to check for surface contamination. The intersection of the solid and liquid surfaces is observed through a microscope which has a 32-mm. objective, and an eyepiece with a fixed vertical crosshair and a traveling horizontal crosshair.

The temperature coefficient of the contact angle of pure water on either graphite or paraffin is +0.06° per degree C. Therefore temperature control of better than plus or minus one or two degrees is unnecessary, so the room temperature was kept between 23 and 27° while taking measurements for calculations at 25°. A metal box with a glass window for observation was kept over the trough and slide during measurements in order to keep out air currents and contamination from the air.

**Measurement of Surface Tension.**—The surface tension of most of the aqueous solutions was measured with the Wilhelmy[2] balance. An ordinary balance can be adapted for this purpose. Weights were put in one pan to counterbalance the pull of a vertical thin glass slide suspended from the other balance arm. This glass slide passed through the surface of the liquid contained in the trough. The knife edges were razor blades and the bearings were of agate. The glass slide was a 35 mm. by 60 mm. no. 1 cover glass.

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[1] C. G. Sumner, "Wetting and Detergency," Chemical Publishing Company, New York, N. Y., 1937, p. 41.

[2] Wilhelmy, *Ann. Physik*, **119**, 177 (1863); A. Frumkin, *Z. physik. Chem.*, **116**, 466 (1925); Harkins and Anderson, THIS JOURNAL, **59**, 2189 (1937).

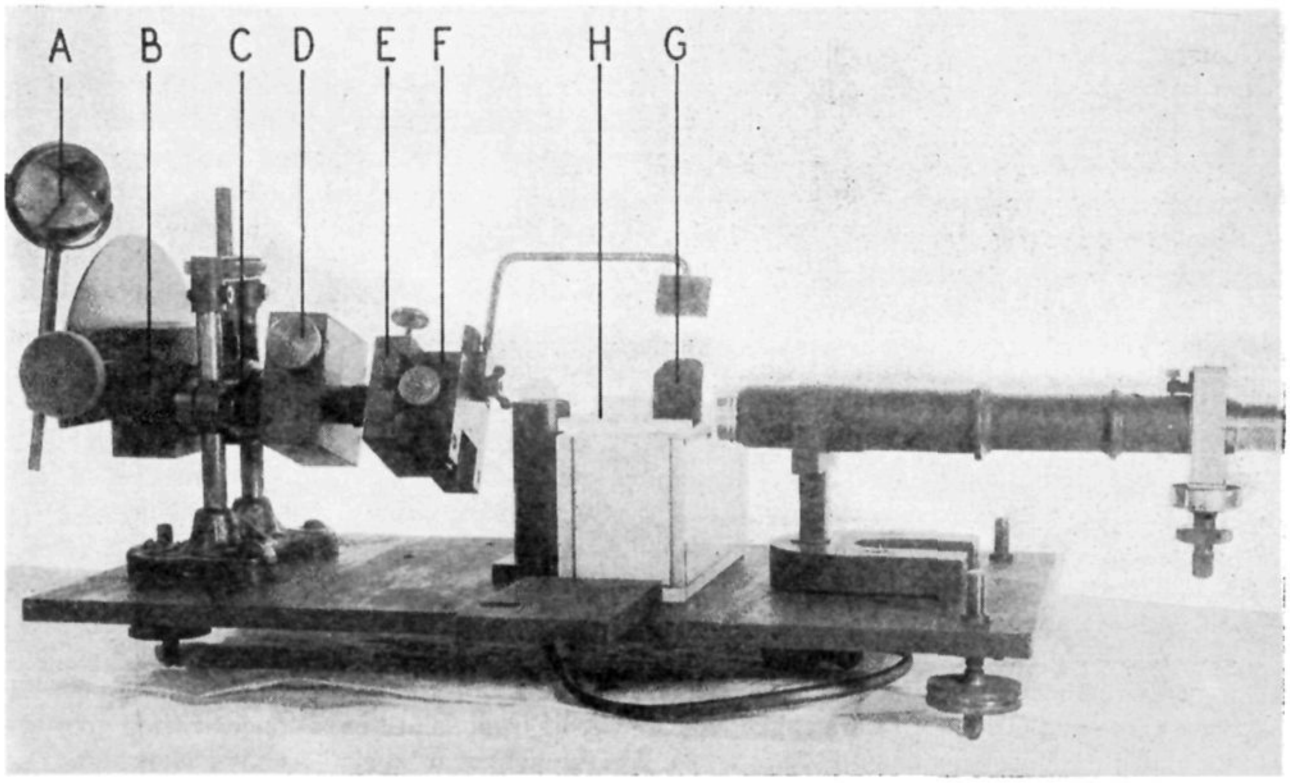

Fig. 2.—Instrument for the measurement of contact angles.

When the pointer of the Wilhelmy balance has been brought to the zero point during a surface tension measurement, the equation for the balance may be written

$$W = f(H) + \gamma \cdot p \cos \Theta$$

where $W$ is the weight in dyne cm.$^{-1}$, $f(H)$ is a function of the depth to which the slide is immersed, $p$ is the perimeter of the glass slide where the water surface meets it, $\Theta$ is the contact angle of the solution on glass, and $\gamma$ is the surface tension of the solution. This particular balance and the experimental procedure were so arranged that $f(H)$ was always the same when the balance was balanced. If the masses on the pan equal $M_W$ with pure, freshly-swept water and equal $M_C$ with solution C, the surface tension of solution C is

$$F_C = -\Delta\gamma_C = \frac{(M_W - M_C)}{p} \cdot g$$

provided the contact angles are zero. The $\Theta$ in the above equations was zero for most of the solutions, but with solutions of *n*-butylamine it became as large as 30°, so for these solutions the drop-weight method for the measurement of surface tension[3] was used, since it is independent of the contact angle. The surface tensions as measured by either method are estimated to be accurate to one-tenth of a dyne per centimeter.

## 4. Preparation of Materials

**Surfaces of Solids.**—The solids used in this work were talc, stibnite, graphite and paraffin wax. The surfaces had to be as flat and smooth as it was possible to obtain. All specimens were used as soon as possible after the preparation of their surfaces, and after each measurement the surfaces of the minerals were washed with ethyl alcohol, then with water, and dried under vacuum in a desiccator. The specimens were stored in the desiccator under vacuum until they were needed again.

The paraffin wax was prepared from an ordinary commercial product. It was refluxed for five hours with liquid sodium, and then slowly distilled through a long fractionating column at three millimeters of mercury pressure. The fraction collected for use had a boiling range of 210–220°. Cold clean micro-slides were dipped quickly in and out of the melted paraffin. This gave a smooth even coat which solidified in less than a second, thus preventing much migration of contamination to the surface. The contact angles of pure water on these slides of paraffin varied from 108.8° to 111.0°, but for *each particular specimen* the average deviation from the mean was no larger than 0.2° (see Tables I and II).

The graphite surface was prepared on a slab of Ceylon graphite. After making a flat surface with various grades of emery cloth, and polishing it smooth with a leather hone, the final polishing was done with a fine filter paper. The surface was washed with ethyl alcohol to remove surface active material, and after the customary drying the slide was ready for use. Contact angles of pure water with this graphite surface varied from 85.3 to 85.9°.

A smooth and flat surface of stibnite was prepared by cleaving a large crystal from Iyo, Japan, in the 010 plane. The cleavage was achieved by a tearing action in which the two sides of the crystal were pulled apart. Contact angles of pure water on this surface varied from 84.2 to 84.0°.

Sea-green talc from Rhode Island was also cleaved by a tearing action. Contact angles of pure water on talc varied from 88.0 to 88.6°.

**Solutions.**—Aqueous solutions of *n*-butyl alcohol, *n*-butylamine, *n*-butyric acid, propionic acid, acetic acid and

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[3] Harkins and Brown, THIS JOURNAL, **41**, 499 (1919).

sodium *n*-butyrate were used. The activity of each solution was computed from the activity coefficients.[4] As there are not sufficient data available to calculate the activities at 25° for most of the compounds, the activity coefficients at the freezing point were used. In the case of acetic acid the necessary heats of dilution and specific heats are known, and the activity coefficients were calculated for 25°. The change in the relative values of the activities from the freezing point to 25° changed the *F*–log $a_2$ curve less than would an error in contact angle measurement of 0.1°.

The water used in making up the solutions was distilled twice and showed no observable surface contamination.

Eastman Kodak Co. best grade of *n*-butyl alcohol was distilled through a long fractionating column, and a half degree fraction (117.5–118.0°) was collected for this work.

The propionic and acetic acids were distilled and fractionated and half degree fractions were collected for use. The *n*-butyric acid was Kahlbaum best synthetic product and was used without further purification. The activity coefficients of these three aliphatic acids were taken from the work of Jones and Bury.[5]

Sodium *n*-butyrate solutions were made by neutralizing Eastman Kodak Co. best butyric acid with an aqueous solution of Mallinckrodt Reagent Quality sodium carbonate to a faint pink with phenolphthalein. At this *p*H the butyric acid concentration is so low as not to affect the surface tension to a measurable degree.

Eastman best grade of *n*-butylamine (b. p. 76–78°) was used without further purification. As the activity coefficients of *n*-butylamine are not available in the literature, they were determined by the freezing point method. Since the activity data need be accurate to no more than 1%, the Beckmann method of freezing point measurement was employed. The undercooling correction was applied to obtain the correct depression of the freezing point for the solutions. The activity coefficients were calculated by the method of Lewis and Randall.[6] The standard state was that of a 0.4 molal solution instead of one infinitely dilute. The data for the activity coefficients ($a_2/m$) at the freezing point are given in Table I.

TABLE I

ACTIVITY COEFFICIENTS OF *n*-BUTYLAMINE

| *m* | Freezing point depression, °C. | | $a_2/m$ |
|---|---|---|---|
| 0.0532 | 0.108 | 0.110 | 1.000 |
| .1133 | .227 | .227 | 0.997 |
| .2080 | .403 | .399 | 0.999 |
| .4393 | .817 | .821 | 1.000 |
| .8510 | 1.565 | 1.566 | 0.985 |
| 1.824 | 3.278 | 3.270 | 0.934 |

## Procedure

The contact angle can be used for calculating the film pressure only if the solid–gas tension ($\gamma_{SV}$) remains constant when solutions of all of the different concentrations used in the measurement of the contact angle are present. Therefore in every case studied this equality must be tested. This was done by *saturating* the air over the trough with the vapor from the particular aqueous solution of the organic solute and then measuring the advancing contact angles of pure water on the solid surface in question. The organic molecules which are captured by the surface of the water diffuse into the interior, leaving such a dilute film that the film pressure is not materially affected. Those caught by the solid surface are insoluble in the mineral substances used, so they cannot escape from the surface by this process. The result is that equilibrium is established much more rapidly with the surface of the solid than with that of the liquid. Even with a 1 molal solution there are 55 molecules of water to one of organic material, and the water alone decreases the free surface energy of the solid. If it does this because volatile organic vapors are adsorbed, the contact angle of pure water on the solid will increase. No such increase was discovered except with the more concentrated *n*-butylamine solutions on talc and graphite. Here the effect was noticeable with vapors from solutions of concentration greater than 0.0707 *m*, so *in these cases the data were not used.*

The measurements of surface tension and contact angle are made consecutively in the same trough. The surface of the solution is well swept before the clean wet slide of the Wilhelmy balance is lowered into it. The level of the liquid is adjusted to a standard height which is checked by the scale in the eyepiece of the microscope. Weights are added to the balance pan to bring the pointer to the zero position, and the surface tension is computed. With the balance still in place, the contact angle is measured. Any further drop in surface tension indicating surface contamination is easily noted and the measurement repeated after the surface is cleaned.

The slide of solid (microscope slides support the graphite, talc and stibnite crystals, which are attached by paraffin) is put in place and its angle with the water surface is calibrated at 90°. This is done by setting the pointer at 90° on the protractor scale and turning the calibrating worm until the solid surface is parallel to the vertical cross-hair in the microscope eyepiece. To find the contact angle, the slide is rotated by means of the rotating worm until the water surface lies perfectly flat and horizontal up to the solid surface. The angle shown on the protractor is then the contact angle. A slight shaking of the surface of the water assists in bringing it to equilibrium, although this equilibrium can also be attained by waiting a few minutes. The smoother the solid surface, the sooner equilibrium is attained. With each solution six to twenty contact angles were measured. The solid surfaces are exposed at different points for each measurement by moving the slide up or down by means of the dipping movement. The results are recorded as the average angle plus or minus the average deviation.

In almost every case studied there was found to be no difference in the contact angle whether the slide was advancing or receding. Rough surfaces exhibited lower receding angles, but on smoother parts of the same surface this effect disappeared. Many data in the literature record differences in the advancing and receding angles, but the present

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[4] W. D. Harkins and R. W. Wampler, THIS JOURNAL, **53**, 850 (1931).

[5] Jones and Bury, *Phil. Mag.*, [7] **4**, 481 (1927).

[6] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Company, New York, N. Y., 1923, p. 286.

work indicates that more careful experimental work will eliminate many such differences.

From the experimental data for $\gamma$ and $\Theta$ for each solution, the values of the film pressure ($F$) are calculated and plotted against the logarithm of the activity (log $a_2$). From the slopes of this curve the area per molecule is calculated by the use of the Gibbs adsorption equation.

Table II

Pressure–Area ($FA$) Relations of Monolayers on the Surface of Aqueous Solutions

| $m$ | Log $a_2$ | $\gamma$ | $F$ | $A^a$ | $\Gamma \times 10^{-13}$ molecules cm.$^{-2}$ |
|---|---|---|---|---|---|
| | | *n*-Butylamine (25°) | | | |
| 0 | ..... | 72.0 | 0 | ... | 0 |
| 0.0120 | −1.922 | 70.2 | 1.8 | 169.5 | 5.9 |
| .0273 | −1.563 | 67.3 | 4.7 | 75.4 | 13.3 |
| .0532 | −1.274 | 62.5 | 9.5 | 53.1 | 18.7 |
| .1133 | −0.946 | 56.3 | 15.7 | 40.6 | 24.0 |
| .2080 | − .682 | 49.7 | 22.3 | 37.4 | 25.7 |
| .4393 | − .357 | 41.6 | 30.4 | 34.0 | 26.6 |
| .8510 | − .077 | 33.7 | 38.3 | 31.0 | 28.5 |
| 1.824 | .231 | 28.5 | 43.5 | | |
| | | Acetic Acid (25°) | | | |
| 0 | ..... | 72.0 | 0 | ... | 0 |
| 0.0386 | −1.405 | 71.8 | 0.2 | 338 | 3.0 |
| .1929 | −0.696 | 69.0 | 3.0 | 123 | 7.9 |
| .4048 | − .376 | 65.9 | 6.1 | 74.2 | 12.4 |
| .7925 | − .093 | 61.7 | 10.3 | 41.3 | 22.0 |
| 2.102 | .297 | 52.9 | 19.1 | 33.5 | 24.1 |
| 4.172 | .543 | 47.6 | 24.4 | 27.5 | 24.1 |
| 8.59 | ..... | 42.4 | 29.6 | .. | .. |
| 19.48 | ..... | 36.9 | 35.1 | .. | .. |
| | | Sodium *n*-Butyrate (25°) | | | |
| 0 | ..... | 72.0 | 0 | | |
| 0.0814 | −1.089 | 71.4 | 0.6 | | |
| .1411 | −0.850 | 71.1 | 0.9 | | |
| .296 | −0.529 | 69.9 | 1.9 | | |
| .569 | −0.245 | 67.6 | 4.4 | | |

[a] The molecular area $A$ given in these tables is slightly smaller than the area $A_a$ per molecule adsorbed from solution as given by the equation of Gibbs, since it is obvious that some solute would be in the surface if there were no adsorption. The number of molecules already present in unit area before adsorption occurs has been taken as $n^{2/3}$, where $n$ is the number of solute molecules per cc. This assumption becomes less accurate for very concentrated solutions, but those used in the present investigation are, on the whole, dilute. Data similar to the above are given for *n*-butyl alcohol at 20°, and a few data for propionic and butyric acids at 0°, by Harkins and Wampler, This Journal, **53**, 850 (1931). Almost all of the other values of the adsorption of organic solutes found in the literature are incorrect, since the erroneous assumption is made that the activity and the concentration are equal. Harkins and Wampler show that with *n*-butyl alcohol in water the activity coefficient at 1 molal has a value of only 0.823.

Table III

Pressure–Area ($FA$) Relations at the Interface between Solid Paraffin and an Aqueous Solution

| $m$ | Log $a_2$ | $\gamma$ | $\Theta$ | $F$ | $A$ | $\Gamma \times 10^{-13}$ molecules cm.$^{-2}$ |
|---|---|---|---|---|---|---|
| | | | *n*-Butyl Alcohol (22°) | | | |
| 0 | ..... | 72.4 | 111.0 ∓ 0.2° | 0 | ... | 0 |
| 0.00674 | −2.175 | 72.0 | 109.7 ∓ .2° | 0.7 | 256 | 3.9 |
| .01629 | −1.795 | 69.5 | 109.2 ∓ .1° | 2.7 | 144 | 6.9 |
| .02959 | −1.541 | 66.5 | 108.5 ∓ .1° | 4.8 | 80.7 | 12.4 |
| .0606 | −1.237 | 60.7 | 105.7 ∓ .1° | 9.5 | 47.0 | 21.2 |
| .1222 | −0.943 | 53.5 | 100.1 ∓ .2° | 16.5 | 35.0 | 25.9 |
| .2269 | − .687 | 46.4 | 91.6 ∓ .3° | 24.6 | 28.9 | 33.9 |
| .4565 | − .400 | 37.0 | 78.0 ∓ .4° | 33.6 | 26.4 | 36.5 |
| .8180 | − .165 | 29.2 | 55.3 ∓ .5° | 42.3 | 24.0 | 40.9 |
| | | | *n*-Butylamine (25°) | | | |
| 0 | ..... | 72.0 | 110.9 ∓ 0.2° | 0 | ... | 0 |
| 0.00342 | −2.466 | 71.8 | 109.3 ∓ .2° | 2.0 | 179 | 5.6 |
| .00688 | −2.162 | 71.2 | 107.5 ∓ .3° | 4.3 | 113 | 8.9 |
| .01196 | −1.922 | 70.2 | 105.8 ∓ .2° | 6.6 | 84.8 | 11.8 |
| .02734 | −1.563 | 67.3 | 102.0 ∓ .2° | 11.7 | 57.9 | 17.3 |
| .05323 | −1.274 | 62.5 | 98.6 ∓ .2° | 16.4 | 46.9 | 21.2 |
| .1133 | −0.946 | 56.3 | 92.3 ∓ .2° | 23.4 | 39.5 | 25.0 |
| .2080 | − .682 | 49.7 | 85.3 ∓ .1° | 29.8 | 35.2 | 27.4 |
| .4393 | − .357 | 41.6 | 71.2 ∓ .9° | 39.1 | 31.7 | 29.5 |
| .8510 | − .077 | 33.7 | 51.0 ∓ .6° | 46.9 | 28.8 | 30.3 |
| | | | *n*-Butyric Acid (25°) | | | |
| 0 | ..... | 72.0 | 108.8 ∓ 0.3° | 0 | ... | 0 |
| 0.01068 | −1.889 | 69.6 | 107.5 ∓ .2° | 2.3 | 122 | 8.2 |
| .01753 | −1.674 | 68.1 | 106.4 ∓ .3° | 4.0 | 91.9 | 10.8 |
| .03504 | −1.374 | 64.7 | 103.9 ∓ .1° | 7.7 | 65.7 | 15.1 |
| .0707 | −1.072 | 59.9 | 100.3 ∓ .4° | 12.5 | 46.8 | 21.2 |
| .1280 | −0.819 | 53.9 | 94.3 ∓ .3° | 19.2 | 38.2 | 26.0 |
| .2476 | − .542 | 47.3 | 81.0 ∓ .3° | 26.2 | 31.0 | 31.8 |
| .5412 | − .226 | 38.0 | 67.9 ∓ .5° | 37.5 | 27.6 | 35.4 |
| | | | Propionic Acid (25°) | | | |
| 0 | ..... | 72.0 | 109.9 ∓ 0.2° | 0 | ... | 0 |
| 0.0327 | −1.437 | 69.9 | 108.0 ∓ .1° | 2.9 | 137 | 7.3 |
| .0687 | −1.117 | 67.9 | 106.5 ∓ .3° | 5.2 | 98 | 10.1 |
| .1253 | −0.858 | 65.0 | 104.1 ∓ .2° | 8.7 | 73 | 13.5 |
| .2592 | − .550 | 60.4 | 100.9 ∓ .1° | 13.1 | 50.7 | 19.3 |
| .547 | − .240 | 53.7 | 95.2 ∓ .2° | 19.6 | 37.0 | 25.6 |
| 1.408 | + .127 | 43.9 | 83.5 ∓ .4° | 29.5 | 27.5 | 32.7 |
| 2.193 | + .280 | 40.2 | 75.9 ∓ .5° | 34.3 | 25.8 | 32.7 |
| 4.45 | + .469 | 35.3 | 67.3 ∓ .6° | 38.1 | 23.2 | 32.7 |
| | | | Acetic Acid (25°) | | | |
| 0 | ..... | 72.0 | 108.2 ∓ 0.3° | 0 | ... | 0 |
| 0.0386 | −1.405 | 71.8 | 106.8 ∓ .6° | 2.0 | 436 | 2.2 |
| .1929 | −0.696 | 69.0 | 104.3 ∓ .5° | 5.5 | 111 | 8.5 |
| .4048 | − .376 | 65.9 | 102.1 ∓ .7° | 8.9 | 61.0 | 15.5 |
| .7925 | − .093 | 61.7 | 97.8 ∓ .3° | 14.1 | 48.6 | 18.5 |
| 2.102 | + .297 | 52.9 | 91.5 ∓ .4° | 21.1 | 40.0 | 19.3 |
| 4.172 | + .543 | 47.6 | 85.9 ∓ .4° | 25.9 | 31.4 | 20.5 |
| 8.59 | ..... | 42.4 | 78.2 ∓ .4° | 31.1 | ... | .. |
| 19.48 | ..... | 36.9 | 70.2 ∓ .2° | 35.1 | ... | .. |
| Pure solute | | 26.9 | 44.0 ∓ 1.0° | 42.0 | ... | .. |
| | | | Na *n*-Butyrate (25°) | | | |
| 0 | ..... | 72.0 | 109.5 ∓ 0.1° | 0 | | |
| 0.01522 | −1.818 | 72.1 | 109.1 ∓ .3° | 0.4 | | |
| .0369 | −1.433 | 72.0 | 108.3 ∓ .1° | 1.4 | | |
| .0814 | −1.089 | 71.4 | 108.2 ∓ .3° | 1.7 | | |
| .1411 | −0.850 | 71.1 | 106.5 ∓ .2° | 3.8 | | |
| .296 | − .529 | 69.9 | 105.7 ∓ .3° | 5.1 | | |
| .569 | − .245 | 67.6 | 103.5 ∓ .1° | 8.2 | | |

## 5. Effect of Different Solids and Liquids on the Adsorption and Pressure–Area Relations

The data obtained for the relations of *n*-butyl alcohol, *n*-butylamine, *n*-butyric acid, sodium *n*-

TABLE IV

PRESSURE–AREA (*FA*) AT THE INTERFACE BETWEEN TALC AND AN AQUEOUS SOLUTION AT (25°)

| $m$ | Log $a_2$ | $\gamma$ | $\theta$ | $F$ | $A$ | $\Gamma \times 10^{-13}$ molecules cm.$^{-2}$ |
|---|---|---|---|---|---|---|
| | | | *n*-Butyl Alcohol | | | |
| 0 | ..... | 72.0 | 87.9 ∓ 0.2° | 0 | ... | 0 |
| 0.0135 | −1.876 | 69.0 | 84.6 ∓ .1° | 0.5 | 165 | 6.1 |
| .0330 | −1.493 | 64.3 | 83.2 ∓ .2° | 4.1 | 84.7 | 11.8 |
| .0564 | −1.266 | 60.6 | 80.1 ∓ .3° | 8.3 | 66.7 | 14.9 |
| .1095 | −0.987 | 54.1 | 74.2 ∓ .5° | 12.6 | 55.9 | 17.7 |
| .2297 | − .680 | 45.5 | 64.1 ∓ .4° | 17.8 | 49.0 | 19.3 |
| .4362 | − .418 | 37.0 | 47.7 ∓ .3° | 22.8 | 44.1 | 20.7 |
| .947 | − .107 | 27.5 | 0 | 25.4+ | | |
| | | | *n*-Butylamine | | | |
| 0 | ..... | 72.0 | 87.7 ∓ 0.2° | 0 | ... | 0 |
| 0.00342 | −2.466 | 71.8 | 86.2 ∓ .8° | 1.9 | 141 | 7.1 |
| .00688 | −2.162 | 71.2 | 83.7 ∓ .3° | 4.9 | 82.4 | 12.1 |
| .01196 | −1.922 | 70.2 | 81.1 ∓ .1° | 8.0 | 62.5 | 16.0 |
| .02734 | −1.563 | 67.3 | 75.5 ∓ .5° | 14.0 | 46.5 | 19.9 |
| .05323 | −1.274 | 62.5 | 68.4 ∓ .3° | 20.1 | 42.0 | 24.5 |
| .1133 | −0.946 | 56.3 | 55.7 ∓ .3° | 28.8 | 35.0 | 28.3 |
| .2080 | − .682 | 49.7 | 44.5 ∓ .2° | 32.6 | | |
| .4393 | − .357 | 41.6 | 10 | 38.1 | | |

butyrate, propionic acid, and acetic acid at the interface aqueous solution–vapor are presented in Table II, and those for these substances at the interface between the various solids, in Tables III to VI.

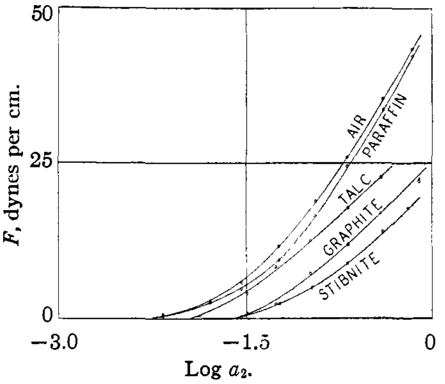

Fig. 3.—Films at various boundaries of *n*-butyl alcohol solutions.

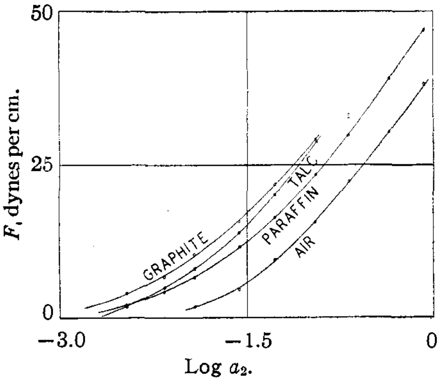

Fig. 4.—Films at various boundaries of *n*-butylamine solutions.

TABLE V

PRESSURE–AREA (*FA*) AT THE INTERFACE BETWEEN STIBNITE AND A SOLUTION OF *n*-BUTYL ALCOHOL (22°)

| $m$ | Log $a_2$ | $\gamma$ | $\theta$ | $F$ | $A$ | $\Gamma \times 10^{-13}$ |
|---|---|---|---|---|---|---|
| 0 | ..... | 72.4 | 84.2 ∓ 0.1° | 0 | ... | 0 |
| 0.02959 | −1.541 | 66.5 | 83.4 ∓ .2° | 0.3 | 186 | 5.4 |
| .0606 | −1.237 | 60.7 | 80.7 ∓ .3° | 2.5 | 122 | 8.1 |
| .1132 | −0.968 | 53.5 | 75.5 ∓ .3° | 4.9 | 80 | 11.9 |
| .2269 | − .687 | 46.4 | 69.7 ∓ .3° | 8.9 | 57.5 | 16.5 |
| .4565 | − .400 | 37.0 | 54.8 ∓ .3° | 14.0 | 45.3 | 20.1 |
| .7609 | − .194 | 29.2 | 33.8 ∓ 1.5° | 17.8 | 42.0 | 20.7 |

TABLE VI

PRESSURE–AREA (*FA*) RELATIONS AT THE INTERFACE BETWEEN GRAPHITE AND AQUEOUS SOLUTIONS (AT 25°)

| $m$ | Log $a_2$ | $\gamma$ | $\theta$ | $F$ | $A$ | $\Gamma$ |
|---|---|---|---|---|---|---|
| | | | Butyl Alcohol Solution | | | |
| 0 | ..... | 72.0 | 85.7 ∓ 0.2° | 0 | ... | 0 |
| 0.0135 | −1.876 | 69.0 | 84.4 ∓ .4° | 1.6 | ... | .. |
| .0330 | −1.493 | 64.3 | 84.5 ∓ .1° | 1.2 | 273 | 3.7 |
| .0564 | −1.266 | 60.6 | 82.5 ∓ .2° | 2.8 | 102.5 | 9.6 |
| .1095 | −0.987 | 54.1 | 76.3 ∓ .2° | 7.7 | 59.0 | 16.8 |
| .2297 | − .680 | 45.5 | 67.5 ∓ .3° | 12.3 | 49.2 | 19.3 |
| .4362 | − .418 | 37.0 | 52.5 ∓ .5° | 17.4 | 44.0 | 20.7 |
| .947 | − .107 | 27.5 | 0 | 22.4 | 38.0 | 22.0 |
| | | | Butylamine | | | |
| 0 | ..... | 72.0 | 85.6 ∓ 0.2° | 0 | ... | 0 |
| 0.00342 | −2.466 | 71.8 | 82.4 ∓ .2° | 4.0 | 129.5 | 7.7 |
| .00688 | −2.162 | 71.2 | 80.1 ∓ .2° | 6.7 | 83.5 | 12.0 |
| .01196 | −1.922 | 70.2 | 76.9 ∓ .1° | 10.4 | 67.5 | 14.8 |
| .02734 | −1.563 | 67.3 | 71.5 ∓ .3° | 15.8 | 51.8 | 19.3 |
| .05323 | −1.274 | 62.5 | 64.1 ∓ .5° | 21.8 | 44.5 | 22.4 |
| .1133 | −0.946 | 56.3 | 52.1 ∓ .7° | 29.1 | 38.8 | 25.3 |
| .2080 | − .682 | 49.7 | 39.2 ∓ .4° | 33.1 | ... | .. |
| .4393 | − .357 | 41.6 | 30.3 ∓ 1.0° | 30.4 | ... | .. |
| .8510 | − .077 | 33.7 | 0 | 28.2 | ... | .. |

Since these are the first data related to the equation of state at a solid–liquid interface, it is important to exhibit the relations and compare them with those at the liquid–air interface. At a constant value of the activity of the solute the film pressure is found to increase in the following order of the interfaces if *n*-butyl alcohol is the solute: stibnite, graphite, talc, paraffin, air (Fig. 3), and in the inverse of this if *n*-butylamine is the solute (Fig. 4). At the interface paraffin–solution Traube's rule is found to hold in just the same way as in the ordinary case of the surface of a solution (Fig. 5). Thus at the solution–paraffin interface $\Delta \log a_2$ is 5.2 between butyric and propionic acid and 4.6 between propionic and acetic acid, while at the solution–air interface the similar values are 5.5 and 5.2. As is to be expected at a given molality the film pressure exhibited by butyric acid is much greater than that given by its alkali salt (Fig. 6).

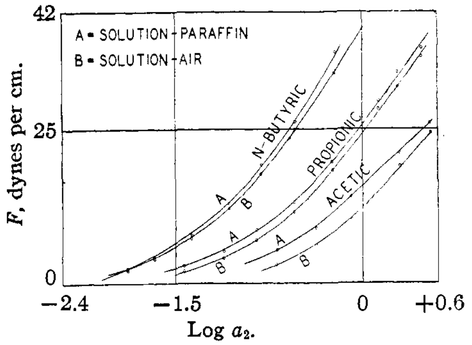

Fig. 5.—Films of fatty acids at two interfaces.

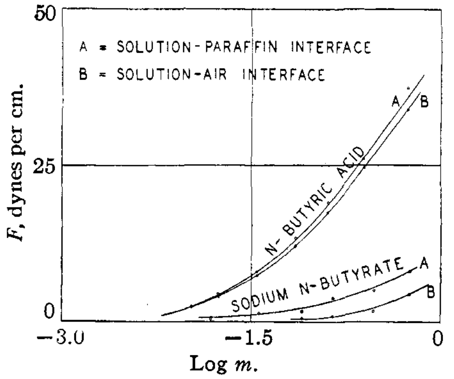

Fig. 6.—Comparison of a salt and its free fatty acid.

That all of the films give pressure–area (*F*, *A*) diagrams closely similar to those exhibited by gaseous films is shown by Figs. 7, 8, and 9.

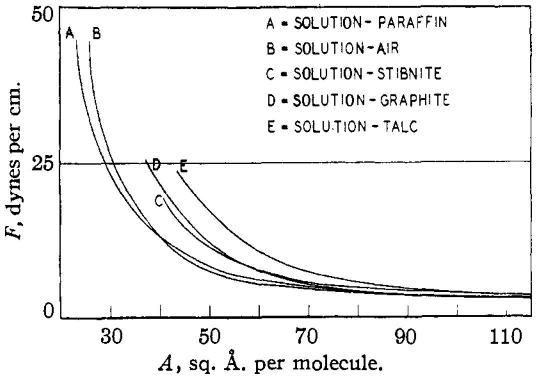

Fig. 7.—*F*–*A* curves for films of *n*-butyl alcohol at various interfaces.

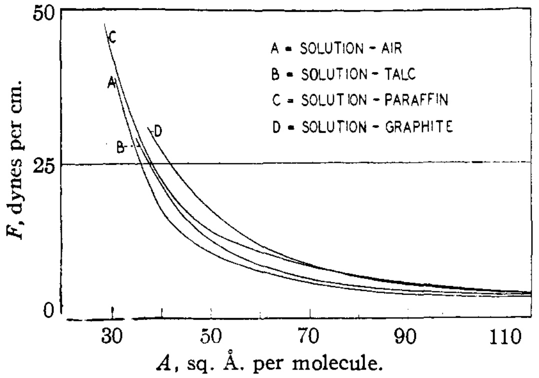

Fig. 8.—*F*–*A* curves for films of *n*-butylamine at various interfaces.

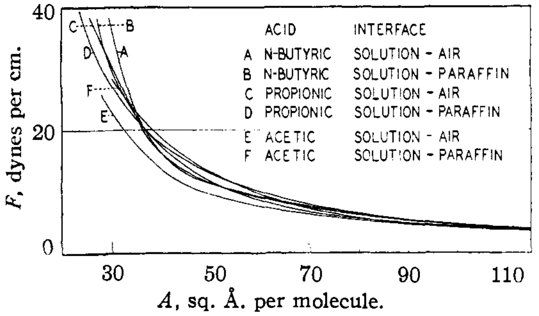

Fig. 9.—*F*–*A* curves for films of three fatty acids at two interfaces.

That the adsorption isotherms are similar to those for various gases with charcoal is shown by Figs. 10 to 12. It is apparent that the upper limb characteristic of the adsorption of multimolecular films of gases on solids is absent. The form of these curves for the adsorption of these solutes at interfaces between an aqueous solution and stibnite, graphite, talc and paraffin, is exactly that obtained in this Laboratory for the adsorption of oleic or stearic acid from their solutions in dry benzene on the surfaces of crystals of titanium dioxide, zirconium dioxide, silicon dioxide, tin dioxide, zinc sulfide, zirconium silicate.[7]

In all of these cases the formation of a second adsorbed molecular layer is prevented by the

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(7) W. D. Harkins and E. Boyd, unpublished work

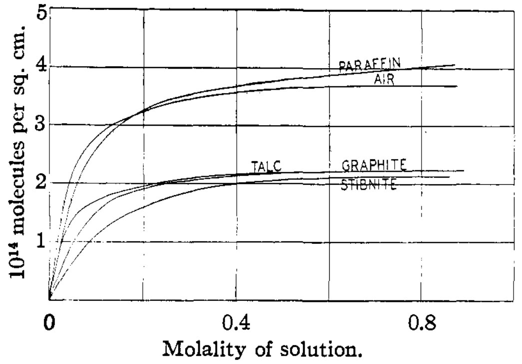

Fig. 10.—Adsorption of *n*-butyl alcohol at various boundaries.

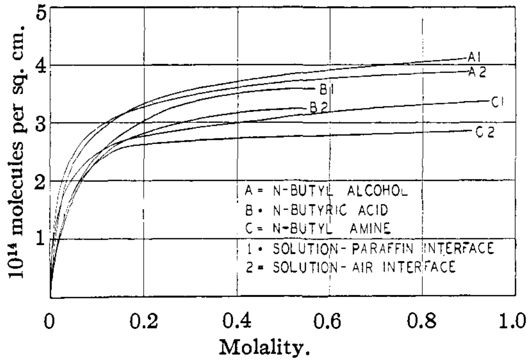

Fig. 11.—Adsorption of three compounds at two interfaces.

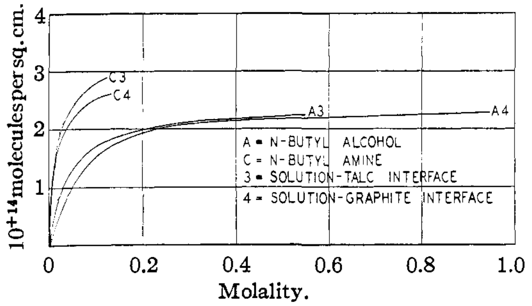

Fig. 12.—Adsorption of two compounds at two interfaces.

presence of the second component, either water or benzene.

In order to bring out the state of the film more clearly the *FA vs. F* relations are exhibited in Figs. 12 to 15. The curves thus obtained are similar to the *PV vs. P* relations of carbon dioxide at not too low pressures. Thus they seem to indicate that these films are in the gaseous state. For a film which is a perfect gas in two dimensions the relation is per molecule

$$FA = kT$$

or at the temperature used in these experiments

$$FA = 400$$

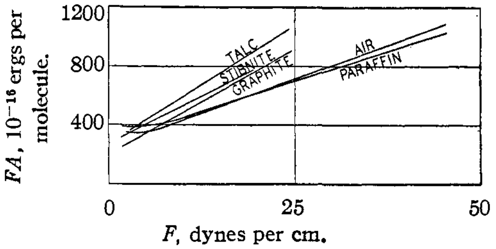

Fig. 13.—Films of *n*-butyl alcohol at various solution boundaries.

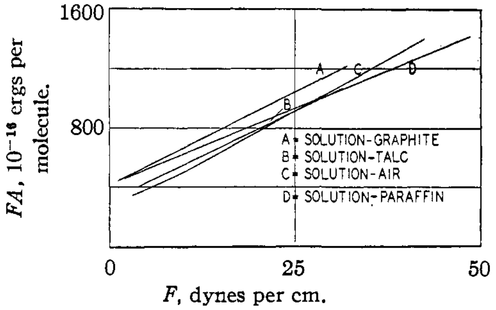

Fig. 14.—Films of *n*-butylamine at various interfaces.

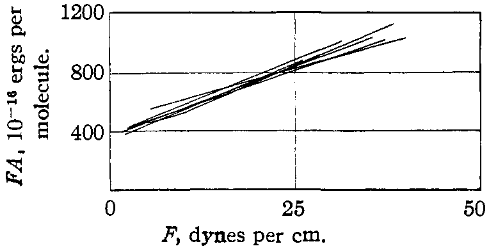

Fig. 15.—Films of three fatty acids at two interfaces.

As is the case with imperfect three dimensional gases the (almost) linear part of the curve extrapolates to a value at zero pressure which is slightly below the theoretical. With films of butyl alcohol at the paraffin–solution interface it was found possible to work at pressures sufficiently low to show that the linear part of the curve, as the pressure is made sufficiently low, begins to turn toward the value 400 (Fig. 13).

## 6. Discussion

Several interesting features have been omitted from the relations described in connection with the figures.

It is found that the interfaces studied fall into two classes: (I) Vapor–liquid, and paraffin–liquid, and (II) stibnite–liquid, talc–liquid, and graphite–liquid. Thus at a given activity or a given film pressure the molecular areas in films of butyl alcohol are much smaller for Class II than for Class I.

Butylamine is much more highly adsorbed than butyl alcohol at the interface of the aqueous solution with either talc or graphite.

The maximum film pressure found in this work was 50 dynes per cm. which corresponds to a three-dimensional pressure of 600 atmospheres.

It was shown in the earlier discussion that the films exhibit in two dimensions the characteristics of an imperfect gas. For such a film the equation of state may be written

$$FA = ckT + eF$$

the values of the constants $c$ and $e$, as calculated from the data by the method of least squares, are given in Table VII.

TABLE VII

CONSTANTS FOR THE EQUATION $FA = ckT + eF$

| Aqueous solution of | Second phase | $c$ | $e$ |
|---|---|---|---|
| *n*-Butyl alcohol | Air | 0.602 | 20.3 |
| *n*-Butyl alcohol | Paraffin | .706 | 17.6 |
| *n*-Butyl alcohol | Stibnite | .652 | 26.8 |
| *n*-Butyl alcohol | Talc | .648 | 34.3 |
| *n*-Butyl alcohol | Graphite | .583 | 29.2 |
| *n*-Butylamine | Air | .593 | 25.9 |
| *n*-Butylamine | Paraffin | 1.012 | 21.5 |
| *n*-Butylamine | Talc | 0.726 | 25.8 |
| *n*-Butylamine | Graphite | 1.033 | 25.2 |
| *n*-Butyric acid | Air | 0.878 | 19.1 |
| *n*-Butyric acid | Paraffin | .955 | 16.7 |
| *n*-Propionic acid | Air | .910 | 17.3 |
| *n*-Propionic acid | Paraffin | 1.280 | 10.1 |
| Acetic acid | Air | 0.762 | 15.4 |
| Acetic acid | Paraffin | 0.875 | 23.1 |

## 7. Monolayers

The energy relations involved in the adsorption of polar–nonpolar (amphipathic) organic substances at the interface between an organic liquid and a hydrophilic, or polar, solid, show very clearly that the film is monomolecular.[8] In the present investigation hydrophobic solids were used with a polar liquid. From the general principles of the orientation theory as stated by Harkins, Davies and Clark,[9] the films formed at such an interface by the substances used, should also be monomolecular.

In a tightly packed monomolecular film of a *n*-long chain paraffin derivative, the smallest area is 20 sq. Å. The smallest areas found at the interface with a solid are: 24 sq. Å. and 23.2 sq. Å. for *n*-butyl alcohol and propionic acid, respectively, with paraffin; 35 sq. Å. for *n*-butylamine with talc; 42 sq. Å. for *n*-butyl alcohol with stibnite, and 38 sq. Å. for butyl alcohol with graphite. These values indicate that the film is not only monomolecular, but also that in most of the cases the concentration of the solution has not been sufficient to form even a *complete* monolayer.

## Summary

1. An improved apparatus has been developed for the determination of the contact angle between a liquid and the plane surface of a solid, by the use of the principle of the tilting plate. One of the greatest advances is the introduction of barriers to clean the surface, and of a small Wilhelmy type film balance to determine the film pressure of the liquid phase, and to show whether the surface of any pure water used is clean.

2. A theory is presented, by means of which it is possible to determine the film pressure ($F$) at the interface between a solid and an aqueous solution of an organic substance. This is possible only if the contact angle between the solid and the solution is greater than zero. No method has yet been found of avoiding an assumption which must be tested experimentally, and which may restrict the use of the method to not too concentrated solutions. The assumption is that the free surface energy of the solid–liquid interface, already greatly lowered by the adsorption of water vapor, is not sufficiently affected by the additional adsorption of the organic substance to materially affect the contact angle. The experimental test of this assumption is described in the text.

3. A considerable advance is made in the determination of the contact angle in the fact that it is found possible, with smooth surfaces, to obtain the same value for the "receding" as for the "advancing" angle.

4. All of the films adsorbed, none of which contained molecules with more than four carbon atoms, were found to be two dimensional, imperfect, gases. The constants of the equation $FA = ckT + eF$ are given in Table VII.

5. Such films exhibit much the same pressure–area relations at the solid–liquid, as at the liquid–vapor interface, in all of the cases investigated.

6. Solutions of the sodium salt of butyric acid are found to be much less capillary active at the solid–solution interface than solutions of butyric acid. This is true for the solids thus far investigated, and is known from earlier work to hold for the liquid–vapor interface.

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[8] W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

[9] W. D. Harkins, E. C. H. Davies and G. L. Clark, THIS JOURNAL, **39**. 541 (1917).

7. The properties of adsorbed films vary according to the type of interface involved. The five interfaces used in this work may be classified as belonging to two different types, the members of either of which are much alike in their effects on films adsorbed upon them. In one group are the solution–air and the solution–paraffin interfaces, and in the other the solution–talc, the solution–stibnite and the solution–graphite interfaces.

8. The pressure–area relations and the wetting characteristics of films of adsorbed organic molecules are highly dependent on the type of polar group in the molecules.

9. A moderate change in the length of the hydrocarbon chain in the adsorbed organic molecule makes little difference in the pressure–area relations, but a great deal in the concentration of the organic compound necessary to give an adsorbed film of any certain film pressure.

10. That the films investigated in this work are monolayers, seems evident. Thus the lowest areas found per molecule are considerably larger than the minimum area in monolayers on the surface of water, which is 20 Å.$^2$ for $n$-long chain paraffin derivatives, and should be somewhat less than this for molecules as small as those of acetic acid.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 27, 1940

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL]

# Preparation and Properties of Serum and Plasma Proteins. I. Size and Charge of Proteins Separating upon Equilibration across Membranes with Ammonium Sulfate Solutions of Controlled *p*H, Ionic Strength and Temperature

BY E. J. COHN, T. L. MCMEEKIN, J. L. ONCLEY, J. M. NEWELL AND W. L. HUGHES

Ever since the beginning of the last century it has been known that blood plasma or serum is a complex system containing a large number of protein components. Certain of these are water-soluble albumins, others are classified as globulins, soluble in neutral salt solutions, but not in water. Separation of globulins from albumins may be effected by dialysis and electrodialysis at reactions close to the isoelectric points of the respective proteins, or by "salting out" methods, ammonium or sodium sulfate or sodium or potassium phosphate being most generally used.[1] Water-insoluble, salt-soluble globulins are largely precipitated by half-saturated ammonium sulfate, whereas the water-soluble albumins require far higher concentrations of neutral salts for precipitation. The ratio of albumins to globulins reported is often the ratio of proteins remaining in solution to those precipitated at half saturation with ammonium sulfate under certain standardized conditions, or some method based on this relation.

The larger part of the protein precipitated by half-saturated ammonium sulfate is not true globulin (euglobulin) in the sense that it is insoluble in water. In the accumulated literature regarding plasma and serum proteins part is, or appears to be, water-soluble pseudoglobulin. Unlike the true serum globulins, the pseudoglobulins cannot be purified by isoelectric precipitation from salt-free solution, and unlike the hemoglobins, haemocuprein and the serum albumins, they have not thus far been prepared in a crystalline state. Like the true globulins and the albumins, pseudoglobulins can, however, be concentrated and purified by repeated reprecipitations by neutral salts.

The solubility of any purified protein in concentrated salt solution is given by the relation $\log S = \beta - K_sC$, where $S$ is the solubility of the protein; $C$, the concentration of the neutral salt sometimes expressed as moles per liter, sometimes as moles per 1000 g. of water; $K_s$, the salting-out constant, a function of the protein and of the neutral salt but independent over wide ranges of *p*H and temperature; and $\beta$, a constant relating change in solubility to change in *p*H.[2] If two proteins of widely different properties are studied, analysis of their solubilities may be effected by means of the above equation. Whereas the solubility of the proteins in serum has been carefully

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[1] (1) Much of the literature on this subject not specifically referred to in this communication is considered in references (2–13)(17)(19)(22) and in the recent studies of H. Wu, *Chinese J. Physiol.*, **7**, 125 (1933); L. F. Hewitt, *Biochem. J.*, **28**, 2080 (1934); **30**, 2229 (1936); **31**, 360 (1937); Goettsch and Kendall, *J. Biol. Chem.*, **109**, 221 (1935); and R. A. Kekwick, *Biochem. J.*, **32**, 552 (1938).

[2] (2) E. J. Cohn, *Physiol. Rev.*, **5**, 349 (1925); *Ann. Rev. Biochem.*, **4**, 93 (1935); *Harvey Lectures*, 124 (1938–1939).