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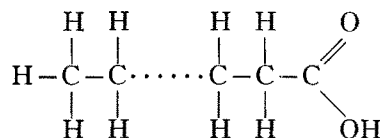
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A new method of studying the electrical properties of monomolecular films floating upon a liquid has been described. Measurements on the potential jump, dV, because of the presence of monomolecular films of oleic acid, palmitic acid, tricaprylin, and trimyristin on water have been made in order to furnish a comparison with the work of Guyot. Excellent agreement was found in all cases. In addition, Guyot's conclusion was verified that dV for fatty acids depends greatly upon the presence of a trace of sulphuric acid in the water while dV for substances like tricaprylin and trimyristin is but slightly affected by the presence of acid.

I. NATURE OF OIL FILMS ON WATER

WHEN a drop of oleic acid or of any one of a large number of insoluble oils is placed on the surface of water, it rapidly spreads out into an invisible film. The early work of Devaux[1] and Pockels[2] demonstrated the existence of these films, while Lord Rayleigh pointed out the likelihood of their being but one molecule thick. By measuring the limiting area of spreading of a previously weighed drop of oil, Langmuir[3] calculated the number of molecules, N, per unit area of the film. Upon comparing the value of N for a number of oils belonging to a homologous organic series, such as the fatty acids, he found it to be the same for all members of the series. It did vary from series to series, however. Thus N for acetates is not the same as N for alcohols. With these data as a basis he showed conclusively that the oil films are but one molecule thick. Ordinarily the molecules of the film are closely grouped together in a single layer much like a layer of marbles grouped together on a table. Long molecules such as higher members of the fatty acid series have the active end, COOH, closest to the water, while the hydrocarbon chain projects approximately at right angles away from the water surface. Thus in the case of stearic acid,

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\cdots\cdots\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{\displaystyle O}{\diagup\!\diagup}}{\underset{\diagdown OH}{C}},$$

the active group $-COOH$ dips into the water, while the hydrocarbon group of 17 carbon atoms projects away from it.

II. THE LANGMIUR MOVING-BARRIER APPARATUS

Langmuir devised an apparatus by means of which the film was compressed at the boundaries by a measured force per unit length, F. A graph of F as a function of N, the number of molecules per unit area of film, showed one or more points of discontinuity in the slope. In Fig. 1 is shown the sort of curve obtained for myristic acid.

N. K. Adam and later E. Rideal and their collaborators[4a, b] elaborated Langmuir's methods and made extensive applications of the $F-N$ curves obtained to the study of monomolecular films and to the analysis of numerous organic structures. The latter application is possible because as N is increased the graph of F against N may exhibit changes of slope caused by rearrangements in orientation of the often complex-shaped molecules in order to be in a state of minimum energy.

[1] H. Devaux, J. de Physique **2**, 273 (1931).
[2] A. Pockels, Ann. d. Physik und Chemie **67**, 668 (1899).
[3] I. Langmuir, J. Am. Chem. Soc. **39**, 1848 (1917).

[4a] N. K. Adam and collaborators, Proc. Roy. Soc. A, 1921 to date.
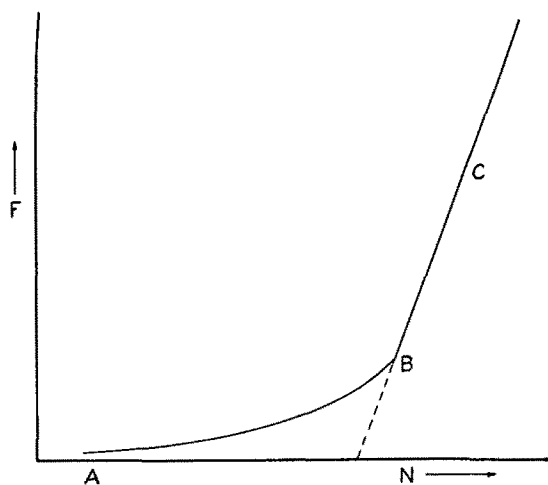[4b] E. Rideal and collaborators, Proc. Roy. Soc. A, 1925 to date.

FIG. 1. Force-area curve for myristic acid at 5C.

III. THE ELECTRICAL PROPERTIES OF MONO-MOLECULAR FILMS

The oils forming monomolecular films appear always to be characterized by the presence in the individual molecule of groups of atoms such as $-OH$, or $C=O$, or $C\equiv N$, known to possess electrostatic moments. Because of the parallel orientation of the molecules in the film we may find it possible to measure the electrical moments of individual molecules by studying the electrical field about the film.

If the component of the electrical moment of the molecule perpendicular to the surface of the water is u, and if dV is the change in potential in passing through the film, a well-known theorem of potential theory states that $dV=4\pi uN$.

In order to measure dV, M. J. Guyot[5] developed a method due to Righi[6] which had previously been used to measure the Volta potential difference between two metals. The two metal electrodes separated by an air gap are in series with a sensitive electrometer and a potentiometer. The air space between is radiated with alpha-particles from some radioactive substance. The alpha-particles ionize the gas, and because of the electrical field between the electrodes set up by the Volta electricity the ions migrate to the electrodes causing an electrometer deflection. By adjusting the potential until no electrometer deflection occurs, one measures the Volta potential difference. Guyot first measured the potential difference between water and a metal electrode held in the air just above the surface of the water. He next measured the potential difference when the water was covered by an oil film. The difference between the two measurements was regarded as the potential jump in passing through the oil film.

Schulman and Rideal[7] and later Adam and Harding[8] measured dV with an apparatus similar to that of Guyot. They found the graphs of dV against N to be of great value in the study of monomolecular films. Hughes[9] found it an interesting tool for the study of proteins, and recently Fosbinder and Lessig[10, 11] applied this technique to the study of stearolactone and a number of proteins such as pepsin, casein. They have also indicated a possible application to the study of enzyme reactions.

As might have been expected, the moments u computed from $dV=4\pi uN$ are always less than those found by applying the Debye theory to the temperature variation of the dielectric constant of gases. The polar molecules of water nearest the oil film orient, too, causing the observed dV to be due to the combined effect of the oriented molecules of the film and the oriented water molecules. The water molecules orient with their electrical axes directed opposite to those of the oil molecules. Hence the observed dV is smaller than that caused by the oil film alone, and consequently the computed polar moments are too small. Although as yet it has not been possible from the measurement of dV to obtain true moments, it has been found that substances of large moments have large values of dV. Also, as N is increased by increasing F with the Langmuir apparatus, we can study the effect of closer packing of the molecules on the measured dV, and thus can arrive at interesting conclusions concerning the presence and relative positions of the polar groups within the molecules.

[5] H. Guyot, Ann. de Physique 10, 508 (1924).

[6] Righi, J. de Physique 2, 7, 153 (1888).

[7] Schulman and Rideal, Proc. Roy. Soc. A130, 259, 431 (1931).

[8] Adam and Harding, Proc. Roy. Soc. A138, 411 (1932).

[9] A. Hughes, Trans. Far. Soc. 29, 211 (1933).

[10] Fosbinder and Lessig, J. Frank. Inst. 215, 425 (1933).

[11] Fosbinder and Lessig, J. Frank. Inst. 215, 572 (1933).

The method of Guyot suffers from several faults, the most serious of which are the bother of dealing with radioactive substances and sensitive electrometer and the difficulty of obtaining adequate electrical insulation for use with a sensitive electrometer when maintained near a water bath.

IV. THE EXPERIMENTAL APPARATUS

The method to be described is essentially that previously developed by one of us[12] and later used by us[13] to study the Volta potential difference between a gold electrode and a cleaved single crystal of zinc.

The electrical arrangement employed is shown in Fig. 2. The two metals A and B whose Volta
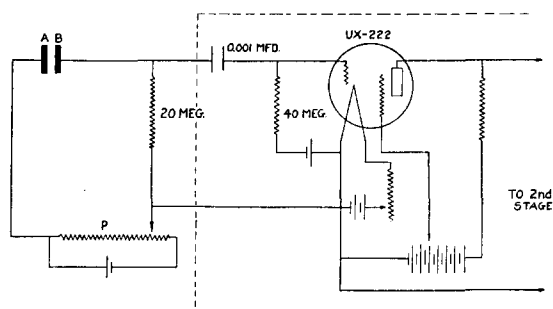
FIG. 2. Electrical circuit diagram.

potential difference is desired are arranged to form a parallel-plate condenser, the capacity of which is changed periodically by varying the separation of the plates. As the potential difference V is independent of the distance between the plates, and the capacity C is a periodic function of the time, and as the charge q on either plate is $q = CV$, there is an alternating current between A and B. This current is detected by connecting in the circuit an audiofrequency amplifier to the output of which a telephone is connected. By adjusting the potential difference applied to A and B by means of the potentiometer until no signal is heard one readily measures the Volta e.m.f., since it is then equal in magnitude and opposite in polarity to the potentiometer reading.

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[12] W. A. Zisman, Rev. Sci. Inst. **3**, 7 (1932).
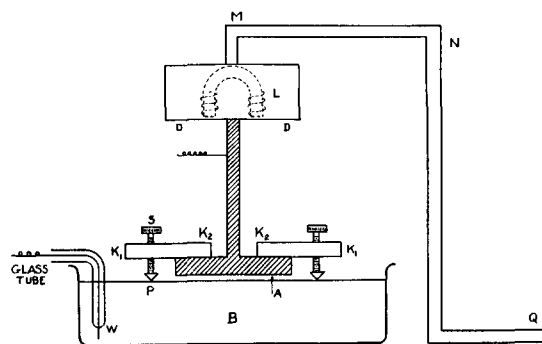[13] W. A. Zisman and H. G. Yamins, Physics **4**, 7 (1933).

FIG. 3. Vibrating condenser for studying Volta effect in liquids.

The experimental arrangement employed to measure dV by this method is shown simply in Fig. 3. A flat gold electrode A is adjusted with its plane parallel to the water surface B. The water, even when prepared in a tin-lined still, is a sufficiently good conductor as compared with the 20-megohm resistance (see Fig. 2) so that a platinum wire, W, dipping into it suffices to make the electrical circuit complete. Of course, it is not a reversible electrode, but that is not needed for the purpose for which this apparatus is designed, since the only requirement this electrode must fulfill is that the potential difference between it and water remain constant for the few minutes needed to make measurements of the potential difference between A and B without and then with the oil film. Electrode A is vibrated to and away from the water surface by attaching it to an insulated rod which is fastened to the center of the flexible diaphragm, DD, of a loudspeaker vibrator, L, such as is used in radio sets. The vibrator was driven by current from a vacuum-tube oscillator at 250–500 cycles per second. It is necessary for high sensitivity to place A as close to the water surface as possible without causing contact. This adjustment is less critical the better the amplifier used. There is no doubt that a much greater gain in amplification can be obtained than that given by our apparatus. We obtained a sensitivity of 0.001 volt in the measurements of dV to be described. With the amplifiers and vacuum tubes now available a much greater sensitivity probably is obtainable.

Several details of technique may prove of interest. The water was contained in a Pyrex tray

about 5 inches in diameter placed upon a miniature three-legged table, one leg of which was capable of a fine screw adjustment so as to vary its height. After the potential difference between the free water surface and gold had been measured, the water surface was removed to a greater distance from the gold by adjustment of the height of the third leg. This permitted addition of the oil film by touching the water surface with a glass rod previously dipped in the oil. Such a procedure prevents chance water ripples from touching the gold electrode. After the addition of the oil film, the table leg was raised in order to make possible the measurement of the potential difference between the oil film and the gold. Three rubber hemispheres were cemented to the upper surface of the table to furnish a stable support for the Pyrex tray.

The adjustment of parallelism between A and B was accomplished by suspending the loudspeaker unit L from a frame MNQ which rested upon three feet Q_1, Q_2, Q_3 of which two, Q_1 and Q_3 were adjustable screws. The Pyrex tray upon Table T was placed as shown in Fig. 4. The plane
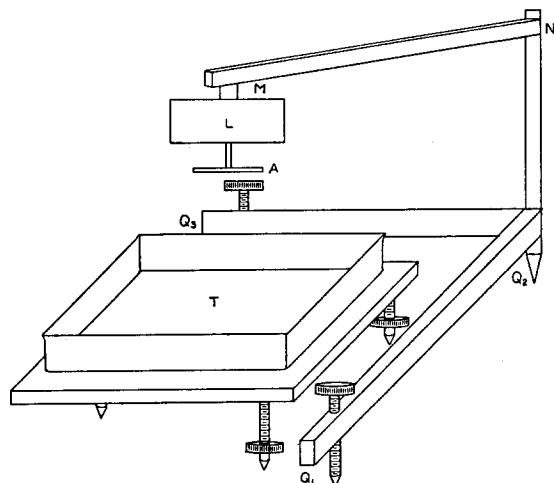

FIG. 4. General arrangement of vibrating condenser and tray.

of A could be easily and finely adjusted by rotation of screws Q_1 and Q_3. It was also found advantageous to have a means of coarse adjustment of the separation and tilt of A and B. We employed a ball and socket joint at the end M of

bar MN and made it so that the length from L to M could be quickly varied about one inch by the sliding of a metal rod in a hole drilled through the ball.

The presence of a convex meniscus at the boundary of contact between water and glass tray makes it impossible to look through the glass side of the tray along the surface of the water and so watch the illuminated slit formed by throwing a beam of light through the air space between the gold electrode and the water. This prevents accurate adjustment of parallelism between A and B when they are quite close. The following was found to be an excellent substitute. Upon the upper surface of the gold electrode are cemented three thin slips of Bakelite KK (see Fig. 3) so that they form three spokes 120 degrees apart. Near the end of each is a fine screw SP, the polished point of which is in the same plane as the under surface of the gold electrode. By tilting the frame MNQ and adjusting the height of the third table leg until each screw point seems about to touch its image reflected in the water, a fine adjustment for parallelism is readily obtained.

The careful electrical shielding of this apparatus is essential. The metal case of the amplifier, the metal housing about the vibrator, L, and the frame MNQ should all be earthed. The wire connecting the electrode B to the grid of the first vacuum tube (see Fig. 2) should be enclosed in a grounded metal cable.

The uniform cleanliness of the gold electrode is important. If the electrode is not clean, the zero intensity of sound is not obtainable, and consequently the ease of measurement is considerably decreased. The electrode was therefore washed occasionally with ether and allowed to dry thoroughly before being used. If the surface of the oil film is not uniform, it is immediately indicated by the poor minimum of intensity of sound at balance. This is a new and valuable feature not possessed by Guyot's apparatus.

The Pyrex tray and platinum wire electrodes were cleaned before each new determination of dV by washing with a strong alkaline solution followed by a solution of potassium dichromate in concentrated sulphuric acid and several final rinsings with grease-free distilled water.

V. RESULTS

(A) Time changes in measurements

The potential difference between gold and water covered with a monomolecular film of oil was found to be independent of the time for intervals ranging up to sixty minutes after formation of the film.

There is a small change with time in the potential difference between the gold and distilled water. It occurs in the first several minutes and amounts to a rise in that time of about 0.005 volt. After that the measurements are constant for twenty or more minutes. With the steady-state value, this potential difference was found to be repeatable to within 0.003 volt usually, provided the water was always obtained from the same still,

If the gold was removed from proximity to the water surface and a few minutes afterwards was brought close again in order to make new measurements, the same sort of rise with time of 0.005 volt occurred. Evidently, this effect must be caused by a slight shift in the potential of the gold due to a condensation of water upon it. Effects of the same order of magnitude were demonstrated to exist in our previous work on the Volta effect in zinc crystals.[13] Blowing water vapor at the newly cleaved crystal caused a rapid shift in the Volta potential difference of about 0.005 volt, but this effect disappeared completely in a few minutes if the condensed water was allowed to evaporate. This effect can be diminished by using greater amplification so as to enable good measurements to be taken with the electrode adjusted further away from the water surface. However, the error in the value of dV is less than 0.005 volt, since the closeness of gold electrode and oil-covered surface prevents evaporation of all the condensed water from the gold.

The values of dV used here were found by employing the steady-state values of the potential differences.

(B) Reproducibility

The values of dV obtained by us were found to be reproducible in a highly satisfactory manner as the following data show. The distilled water was always freshly prepared in a new tin-lined still. The measurements were all made at 22°C.

Three independent runs were made with oleic acid on distilled water. The results were:

Run	1	2	3
dV (volts)	0.163	0.162	0.165

Pure benzene was prepared by triply distilling Kahlbaum's "molecular weight" benzene. Two trial measurements of the potential difference due to dropping this benzene upon water were made. No effect was observed, i.e., $dV=0$, even when the measurements were made as early as 2 minutes after adding the benzene. This proves either that the benzene evaporates without leaving a residue or else that it leaves a residue having no effect on the potential difference between gold and water.

As a further proof that monomolecular films on water may be safely formed by dissolving in benzene the substance to be studied and then placing the solution on the water, the following experiment is cited. Oleic acid was dissolved in benzene and several drops of the resulting solution were placed on distilled water. The resulting dV was 0.164 volt, in excellent agreement with the results given above which were obtained without the use of benzene.

A solution of Eastman palmitic acid in benzene when placed on water gave the following results:

Run	1	2
dV (volts)	0.291	0.298

Using 1/100 normal sulphuric acid instead of the water we obtained:

Run	1	2	3	4	5
dV (volts)	0.380	0.394	0.380	0.383	0.379

Tricaprylin prepared by Eastman was tried on distilled water. The results were:

Run	1	2
dV (volts)	0.407	0.408

It was then studied by using 1/100 normal sulphuric acid in place of the water.

Run	1
dV (volts)	0.426

Trimyristin prepared by Eastman and dissolved in benzene was placed on distilled water. We found $dV=0.612$ volt. With 1/100 normal sulphuric acid in place of the water dV was 0.621 volt.

(C) Comparison with the results of Guyot

In Table I are presented the results of Guyot and ours for the purpose of comparison. His measurements were made at 18°C while ours were at 22°C.

TABLE I.

Substance	dV (Guyot) (volts)	dV (ours) (volts)
Oleic acid on distilled water	0.157	0.163
Palmitic acid on distilled water	0.290	0.295
Palmitic acid on dil. H_2SO_4	0.396	0.383
Tricaprylin on distilled water	0.412	0.408
Tricaprylin on dil. H_2SO_4	0.418	0.426
Trimyristin on distilled water	0.620	0.612
Trimyristin on dil. H_2SO_4	0.618	0.621

Our results are in very good agreement with Guyot's. We also have verified his conclusion that whereas dV for fatty acids is greatly affected by the presence of sulphuric acid, it is but slightly affected for substances like tricaprylin, trimyristin, and trilaurin.