Contact Potentials and the Effects of Unimolecular Films on Surface Potentials. I. Films of Acids and Alcohols

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Simultaneous measurements of film pressure and surface potential have been carried out by the use of an apparatus designed in such a way that the potential may be determined for any location on the surface of the film. At film pressures above that of the gaseous films, organic substances with homo-heteropolar molecules give a single smooth curve for the relation between surface potential and molecular area. At areas sufficiently great to reduce the pressure to that of the gaseous film the surface potential becomes variable and remains variable until the area becomes so great that the continents and islands of condensed film evaporate in the two-dimensional system to give a gaseous film alone. For example with films of myristic acid at 17° the surface potential is represented by a single curve below a molecular area of about 50 sq. Å, and by any value below 170 mv at higher areas, at which islands in the film persist. The areas above which the surface potentials become variable, due to the effects of islands or continents of film, are found to be about as follows: stearic acid, 28; palmitic acid, 28; pentadecylic acid, 41; lauric acid (on NaCl-HCl solution), 36; oleic acid, 52; cetyl alcohol, 23.7; myristyl alcohol, 27. The surface potential rises rapidly with the number of carbon atoms in the hydrocarbon chain, and is about 400 mv for condensed films of stearic acid. It is higher for alcohols than for acids with the same number of carbon atoms. The increment is about that given by the addition of two carbon atoms to the acid. The change of one of the single bonds of stearic acid to the double bond of oleic acid as the film forming substance lowers the surface potential by from 37 to 65 percent, and makes this potential much more greatly affected by the molecular area. The following numbers give the number of carbon atoms in several normal acids and the corresponding potentials at 20 sq. Å at 17°: (12), 276; (14), 336; (15), 375; (16) 383; and (18), 410. The surface potential increases with decrease of temperature, with an increase of concentration in the film, and for the substances investigated, by a replacement of a basic by an acid solution. A collapse of the film lowers the surface potential since it changes the molecular orientation in the film. The films exhibit in the condensed state considerable hysteresis, both with respect to film pressure and surface potential. This feature has not been sufficiently noted in other work. The relation between surface potential and the molecular moments of the molecules which constitute the film is discussed. The dipole moment as calculated from surface potentials by the equation of Helmholtz are only about one-sixth as large as those found by ordinary methods for independent molecules in nonpolar solvents. The discrepancy is attributed partly to a lowering of potential by an orientation of the dipoles with respect to each other, and partly to the too great simplicity of the equation. The apparatus used for this work has been found to give good determinations of the contact potentials of metals. In its design use was made of ideas suggested principally by Lord Kelvin, and by Guyot and by Frumkin.

I. INTRODUCTION

IT has been supposed that the surface of a pure liquid or of a solution is the seat of several different types of potentials. Of these the greatest prominence in the theory of the stability of colloids, as developed by Hardy and later by others, has been given to the electrokinetic or zeta (ζ) potential, the original theory of which was developed by Helmholtz. It has not been found possible to measure the quantity designated by ζ directly as a potential, and it is necessary to introduce relative motion of the phases along the interface if an electromotive force (E) is to be developed, and this appears as a potential difference along and not through the interface. For this reason ζ is sometimes considered as a tangential potential, although it is E, which may have an entirely different order of magnitude, which is measured tangentially.

What may be considered as the contact potential of the surface is less fictitious, since it may be determined by a direct measurement. If the surfaces of two metals are separated by a gas, and if the gas is sufficiently ionized, a potential, known as the contact potential (V) is developed between

the two metals. This particular method for the determination of contact potentials was developed by Kelvin.[1]

What may be designated as the surface potential (ΔV) of a solution was determined in 1883 by Bichat and Blondlot[2] and later by other workers.[3] The method used by Kenrick was to allow the reference liquid to flow down over the inner wall of a moderately large glass tube placed with its axis vertical, and to allow the second liquid to flow from a fine glass tip in a narrow jet down this axis. The two solutions were connected through calomel electrodes to a quadrant electrometer. It is claimed by both Kenrick and Frumkin that this method gives satisfactory results for aqueous solutions of inorganic electrolytes and for not too dilute solutions of derivatives of the hydrocarbons. The errors inherent in the method of the "dropping electrode" are discussed by Williams and Vigfusson.[4]

Unfortunately the values of the surface potentials as determined for similar systems by different observers did not exhibit a good agreement. In an attempt to obtain better values Guyot and Frumkin independently[5] developed a method in which the potential between a metal, coated with a radioactive substance, and a solution, is determined. The method of Guyot and Frumkin was used by Frumkin and Williams[6] and by Schulman and Rideal.[7]

The development of this method did not, however, remove the difficulty that the values obtained by different workers, or even by the same worker, on seemingly identical systems, were extremely variable. The researches on surface films which had been carried on for many years in this laboratory had shown that many films of insoluble organic substances of the polar-nonpolar type are much less homogeneous than had usually been supposed in the literature of the subject. From this point of view it was suggested to Frumkin by one of us (Harkins) in 1928 that the discrepancies would disappear if simultaneous measurements of potential and film pressure were to be taken, the latter by the use of a film balance of the type used by Adam. This suggestion, repeated by Frumkin to Rideal, was the origin of changes in methods abroad, and was taken as the basis of work in the present paper, which agrees remarkably well with that published recently by Adam and Harding.[8] The agreement is as good at low values for the area of the organic molecule as can be expected, especially when the great difficulty of obtaining really pure specimens of normal long chain acids is taken into account. At higher areas all of the difficulties disappear as will be shown later, if the potential is determined for all of the different regions of the film.

Although the relation between the Kelvin-Righi method and that of Guyot and Frumkin seems to have been obscured in the literature of the subject[9] it is obvious that the latter method is the same as the former, with the substitution in the latter of the surface of a solution for that of one of the metals in the former. Thus the potential determined by the method of Guyot and Frumkin is a contact potential. For obvious reasons in the determination of the effect of surface films it is more satisfactory to take the potential of the clean surface as an arbitrary zero, and to consider the change of potential caused by the presence of a film as the surface potential.

A new method for the determination of the contact potential of metals and of the related surface potential of a solution has been devised by W. A. Zisman,[10, 11, 12] who causes the metal elec-

[1] Sir Wm. Thomson, Lord Kelvin, *Mathematical and Physical Papers*, Vol. VI, *Contact Electricity of Metals*, pp. 110 to 145, Cambridge Press, 1911. See also Righi, J. de Physique [2] 7, 153 (1888).

[2] Bichat and Blondlot, J. de Physique [2] 11, 548 (1883).

[3] Kenrick, Zeits. f. physik. Chemie 19, 625 (1896); Guyot, Ann. de Physique (10), 2, 506 (1924); Frumkin, Zeits. f. physik. Chemie 111, 190 (1924); 116, 485 (1925); Garrison, J. Phys. Chem. 29, 1517 (1925); Bühl, Ann. d. Physik [4] 84, 211 (1927); [4] 87, 877 (1928).

[4] Williams and Vigfusson, J. Phys. Chem. 35, 348 (1931).

[5] Guyot, Ann. de Physique [10] 2, 506 (1924). Frumkin, Zeits. f. physik. Chemie 116, 485 (1925).

[6] Frumkin and Williams, Proc. Nat. Acad. Sci. 5, 400 (1929).

[7] Schulman and Rideal, Proc. Roy. Soc. A130, 259, 270, 284 (1930).

[8] Adam and Harding, Proc. Roy. Soc. A138, 411 (1932). See also Schulman and Hughes, ibid. 430 (1932), and Fosbinder and Lessig, J. Frank. Inst. 215, 425 (1933).

[9] See, however, a paper which has appeared since this paper was first written; Whalley and Rideal, Proc. Roy. Soc. A140, 484, 489, 497 (1933).

[10] Zisman, Rev. Sci. Inst. 3, 7 (1932).

[11] Zisman and Yamins, Physics 4, 7 (1933).

[12] Yamins and Zisman, J. Chem. Phys. 1, 656 (1933).

trode to vibrate 250 to 500 times per second instead of coating it with polonium. This method of the vibrating condenser seems to give the same results as that of Guyot and Frumkin, but thus far it has been tested only with respect to the general order of magnitude of the values for the condensed film.

II. APPARATUS AND PREPARATION OF FILMS

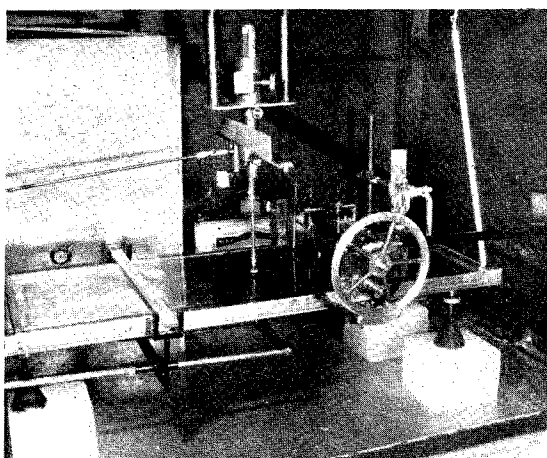The film balance, of the type designed by Adam[13] and modified by Freud and Harkins[14]

FIG. 1. Apparatus for the simultaneous measurement of film pressure and surface potential, and for the determination of the location and contour of continents and islands of condensed film. This view is taken inside the large thermally insulated metal box which surrounds the apparatus. The Compton electrometer is inside the smaller lead box in the left-rear.
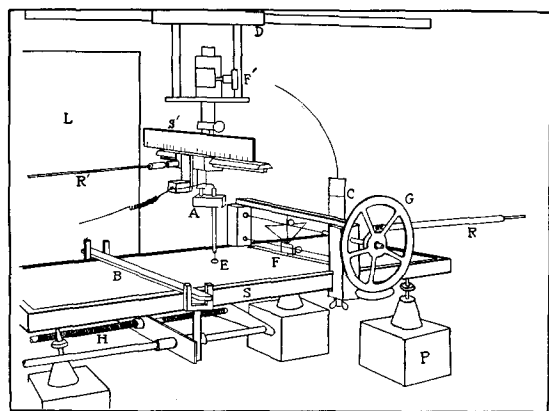

FIG. 2. Diagram of apparatus shown in Fig. 1.

[13] Adam, *Physics and Chemistry of Surfaces*, Clarendon Press, 1930.

[14] Freud, Doctoral Dissertation, University of Chicago, 1927.

(Figs. 1 and 2), is supported on four blocks of paraffin, P, inside a large grounded metal box supported on a heavy concrete pier. Heat insulation of the box is provided by a thick layer of wool felt on the outside. Inside this box is a smaller box L, the inner walls of which are heavy sheets of lead. This box holds the sensitive Compton electrometer used to determine the potential. The electrical circuit is shown in Fig. 3. This is so
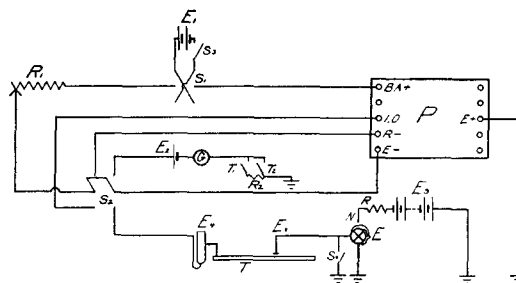

FIG. 3. Diagram of electrical connections for determination of film potential. T, trough of paraffin or brass; P, potentiometer; E_4, one to six calomel cells; E, Compton electrometer; E_1, battery for potentiometer; E_2, standard cell, E_3, battery for charging electrometer; S_2, double-throw double-pole switch: upper position for setting R_1 with P at zero; lower position for measuring E_x on potentiometer with zero reading for E.

arranged that the potential may be either given by a potentiometer, or read directly from the electrometer deflection, which amounts to 680 mm per volt at a scale distance of about 1.5 meters. A much greater sensitivity is easily obtained.

The front of the large box is occupied by two glass doors with metal frames, but the inside of the glass is covered with earthed copper gauze.

As has been customary in this laboratory for many years, the entire operation of the film balance system, except for filling the trough and spreading the film, is carried out by means of handles outside the box. This procedure was also used with the electrical system. Thus the handle on the ebonite rod R controls the film balance, while that connected with the screw H controls the barrier B by means of two forked supports, one at each end of B. A handle on the rod R' serves to shift the position of the silver electrode, coated with polonium, from side to side with respect to the surface of the solution, while the carriage D is moved lengthwise of the film by another rod and handle not shown. Lengths along the

trough are measured by the scale S and those across it by S'. The electrode E is insulated by the amber supports A and its height is adjusted by the rack and pinion F'.

The float F of thin sheet metal is attached to the end supports of the balance by vertical sheets of thin gold shaped as the letter S. The graduated circle G is read by a vernier V below it. The trough T is 25 cm wide and 60 cm long. The surface back of the float F is kept clean by sweeping with various barriers which are not shown. Troughs of glass, paraffin, and of brass carefully coated with paraffin, were found to give results which agree remarkably well.

Preparation of films

The organic acids used for the preparation of the films were the purest that could be obtained. Each sample was washed with a large quantity of pure hot water, and was then recrystallized twice from pure alcohol, and finally dried carefully.

A dilute solution of the film forming substance in a low boiling petroleum ether was prepared. A portion of this solution was put in a special weight pipette designed by Harkins and Freud in 1926. The carefully ground caps and stopper of these pipettes must be kept dry, and if this is done they prevent the evaporation of the solution during the process of weighing. Thus the error of 10 percent in the work of Schulman and Rideal caused by the determination of the amount of solution by counting the drops was avoided. Adam and Harding and Schulman and Hughes have greatly reduced the error below that of Schulman and Rideal by the use of the volumetric pipettes suggested by Fosbinder.

It is obvious that with dilute films the distribution of the islands is highly dependent upon the way in which the drops of the dilute solution are placed upon the surface of the liquid in the trough. An extensive study was made of the effects on the surface potentials of dilute and condensed films as affected by various methods of putting the dilute solution upon the surface.

Electrodes

Many experiments were carried out to determine the best electrode to use with a radioactive substance. A platinum gauze electrode in the form of a small basket with from six to twenty radon tubes laid directly on the metal was found to give potentials which varied (1) with the number of radon tubes, (2) with the distance of the electrode above the surface of the solution, and (3) with the previous treatment of the platinum. For example, the potential in millivolts against the surface of 0.1 molal hydrochloric acid was 95 after immersion of the platinum in cold cleaning solution, -200 after cathodic electrolysis, 312 after anodic electrolysis, and 520 after heating to redness in a Bunsen flame. After standing for several hours the potentials of the electrodes listed above became more nearly the same, but constant results could not be obtained.

Electrodes of various metals covered with polonium were much more satisfactory. Wires and disks of platinum, cadmium, zinc, tin, gold, copper and silver were tried. Good values were obtained with copper but even more constant values with silver, so this metal was used in all of the experiments reported.

Connection with the solution was made by from one to six calomel half cells, which seemed to give better results than a large silver-silver chloride electrode.

III. POTENTIAL AND FORCE-AREA VALUES FOR FILMS OF MYRISTIC ACID

Interesting results were obtained with monomolecular films of myristic acid on 0.01 N hydrochloric acid (Fig. 4), since the curves which give the variation of potential with the mean molecular area of the myristic acid are much more simple than those of Schulman and Rideal.

At molecular areas from 15 to 52 sq. Å the values of the surface potential are represented by a moderately smooth curve. If any inflection at all appears at 32 sq. Å, which is the location of a marked inflection in the pressure-area (FA) curve, it is a very minor one. At areas above 52 sq. Å the pressure falls to that of the gaseous film. The four sets of measurements at areas higher than this are of considerable value in connection with an interpretation of the characteristics of the film. In experiment 1, represented by circles with the lower half inked in, the film was at the beginning very dilute. As the film was compressed from high areas down to 57 sq. Å the potential
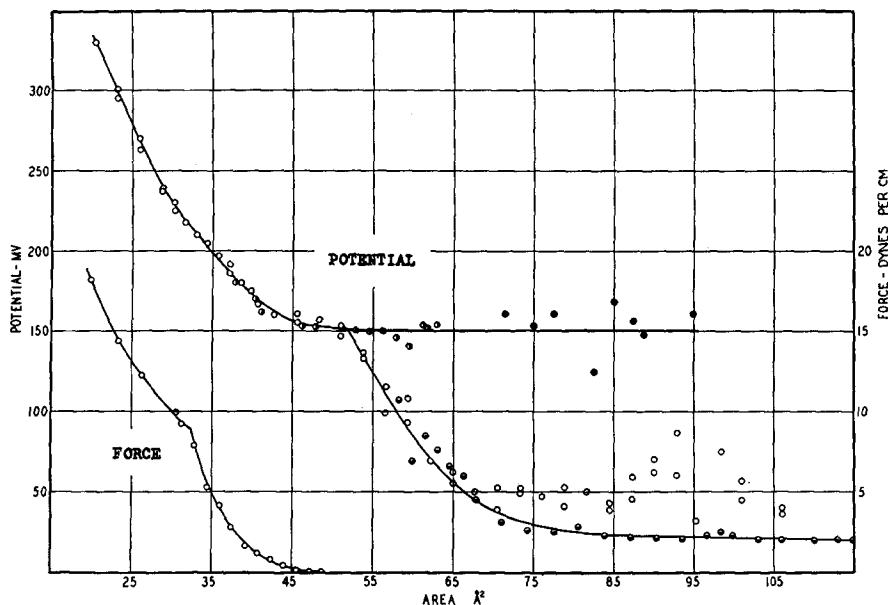
FIG. 4. Lower left = pressure-area relations. Upper right = potential-molecular area relations. Films of myristic acid at 17°. The surface potentials are variable at molecular areas greater than 52 Å. The lower curve corresponds to the potential of a gaseous film, and the higher curve to that for an island.

values increased along a moderately smooth curve. At 115 sq. Å the surface potential was 19 mv, and at 65 sq. Å about 60 mv.

In experiment 2 (open circles), the potentials for areas below 65 sq. Å agree moderately well with those for experiment 1, but at higher areas they vary between 30 and 90 mv. In experiment 3 (black circles) the potentials are much higher, and between 150 and 170 mv. In experiment 4 (left half of circle open) the range of values was more limited, but of the same order as for experiment 4.

In experiments 3 and 4 the silver-polonium electrode was directly over a continent or island of film in what has been called the "expanded" state, which represents a moderately closely packed film. In experiment 1 at 115 sq. Å molecular area the electrode was largely over an area of gaseous film, but the potential was raised by adjacent continents or islands. As the area was decreased the area of gaseous film under the electrode was at first decreased only very slowly, but after the molecular area had decreased to less than 75 sq. Å the continents of concentrated film occupied such a great fraction of the area that further decrease of area caused the gaseous film region to disappear rapidly, with a resultant

rapid increase of potential. However, when the whole film became of the "expanded" rather than of the gaseous type, the rate of increase became much more slow, since the gaseous phase was no longer present, and thus could not disappear.

At areas below 52 sq. Å the pressure was above that of the gaseous film, and the continents of concentrated film were pressed together, so below this area a single curve is sufficient to represent the potential values. However, all irregularities do not always disappear, since the effect of the contour of the continents is not entirely effaced. Between 53 and 22.5 sq. Å for the molecular area the results given in the figure are those of experiments 2 and 3, and are represented by a single smooth curve. Curves of this type were obtained in a considerable number of similar experiments between 10° and 30°. The potential exhibited a general decrease as the temperature was increased. In a few experiments a minor inflection occurred at the same area as that at which the marked inflection occurs in the force-area curve.

A geographic plot of the variation of the surface potential for films of myristic acid at 23° is given in Fig. 5. The variation in potential at the different areas was as follows:

Molecular area in sq. Å	56.5	37.1	25
Minimum potential in mv	0.0	155	238
Maximum potential in mv	176	175	281

In general the variation of the potential decreased as the area decreased toward 20 sq. Å. At 12° Adam and Harding find a variation of 166 mv at a molecular area of 70.6 sq. Å, with a minimum of 1 mv and a maximum of 167 mv.

Palmitic Acid

Area

48 Å²

Barrier→

68	217	315	330
35	59	141	200
233	130	50	61

←Float

282.2 Å²

345	315	324	315
297	310	311	312
319	314	308	305
331	313	313	331

Pentadecylic Acid

48.5 Å²

155	163	170	175
160	20	165	170
165	24	101	170

39.7 Å²

179	183	183	180
179	180	181	180
175	179	180	179
175	179	181	186

Myristic Acid

56.5 Å²

10	22	31	42	90	165	158
0	15	30	38	164	160	156
5	35	51	165	167	165	165
48	98	166	174	171	176	164
145	148	170	169	170	103	199

37.1 Å²

175	170	170	160	157
172	165	168	160	155
169	166	167	164	158
166	169	188	165	155
163	167	190	195	—

25.0 Å²

255	248	255	281
255	248	255	245
255	252	258	243
254	277	261	238
253	254	261	256

FIG. 5. Distribution of surface potential values according to the location of the electrode over the film. The higher values correspond to the more concentrated portions of the film. Barrier on the left, and float attached to film balance on the right. Palmitic acid film at 23°C. Other films at 17°C.

IV. ISLANDS AND OTHER NON-HOMOGENEOUS AREAS IN FILMS

One of the first steps in the work reported in the present paper was to study the effect on the surface potentials at different positions of various methods of dropping the dilute solution of the film forming substance on the surface. For this purpose the silver-polonium electrode was mounted in such a way as to be easily moved in either direction from barrier to float. It was found that when the potential was plotted against the distance a high peak or a wide plateau appeared near the position where a drop had been placed, provided the measurements were made soon after the drops had been deposited. Often, however the islands move quickly from their original positions. The best results are obtained with large islands anchored by some solid object.

The preceding section illustrates the existence of such islands in gaseous films of myristic acid. These appear as floating independent islands at molecular areas higher than those given in Fig. 5, where the islands have largely merged into continents. At extremely great molecular areas the islands disappear or become less prominent.

With a film of palmitic acid at 23° and a molecular area of 48 sq. Å, the surface potential varied from 35 to 330 mv, while at 28.2 sq. Å the potential had become more constant and between 297 and 345 mv. That the potential is not more variable than this is surprising, as the film pressure is still very low. At lower areas and higher pressures the potential becomes still more constant.

With pentadecylic acid the film pressure rises at much higher molecular areas, so that, while at 48.5 sq. Å the potential varies from 20 to 175 mv, at the somewhat high area of 39.7 sq. Å most of the variation has disappeared and the potential varies only from 175 to 180 mv, except in one corner of the film where one value was obtained at 185 mv.

At lower areas than those given in Fig. 5 the potentials in general become more constant and except for some peculiar positions, such as a corner of the film, do not vary more than 3 to 5 mv. However, at molecular areas much below 20 sq. Å the potential again becomes more variable, and in general decreases, since most films crumple at these lower areas, and regions

are produced in which the molecules of the film do not preserve their regular orientation with respect to the surface of the liquid.

V. General Potential Relations for Films of Fatty Acids

The surface potential of a fatty acid film increases rapidly with the length of the hydrocarbon chain. Thus at 20 sq. Å the potentials for stearic (18), palmitic (16), pentadecylic (15), myristic (14), and lauric (12) acids, are respectively 400, 383, 375, 336 and 276 mv.

Each curve in Fig. 6 represents a single experiment. At areas greater than that at which, according to the force-area curves, the pressure apparently falls to zero, other experiments gave other results, but at smaller areas there was good agreement.

The presence of the double bond of oleic acid produces a lowering of about 200 mv, a surprisingly great lowering of the surface potential. The presence of the single double bond lowers

the potential to about the same extent as the removal of six carbon atoms.

The values for myristic acid (14 C) given in Fig. 4 lie below those for pentadecylic acid (Fig. 6). The flat portion of the curve lies at about 150 mv for the former, and 170 mv for the latter.

VI. Alcohol Films

The two higher alcohols investigated (Fig. 7) show the same relation as the acids in that the potential is higher for the alcohol with the longer chain. The surface potential is, however, higher for the alcohols than for the corresponding acids.

VII. Paraffin Layers

Nonpolar hydrocarbons on a clean water surface exhibit different potential relations from a fatty acid. Thus when paraffin was spread from a solution in ligroin, the potential of the interface became 60 mv more positive with respect to the clean surface when the area was decreased to one-fourth the initial area. At the same time the pres-
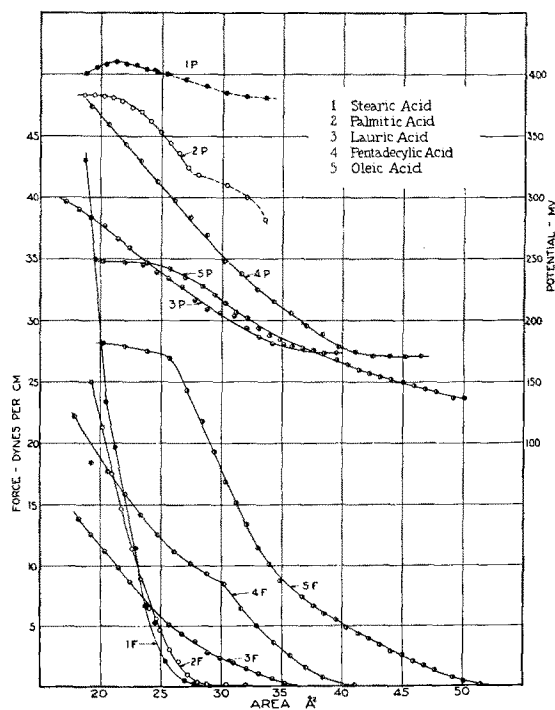

Fig. 6. Surface potentials (*P*) and film pressure values (*F*) for films of organic acids on 0.01 molal hydrochloric acid. The points plotted correspond to individual experiments. The potentials for areas greater than that at which the special force-area curve apparently merges with the *x*-axis, are uncertain. Temperature, 17°.
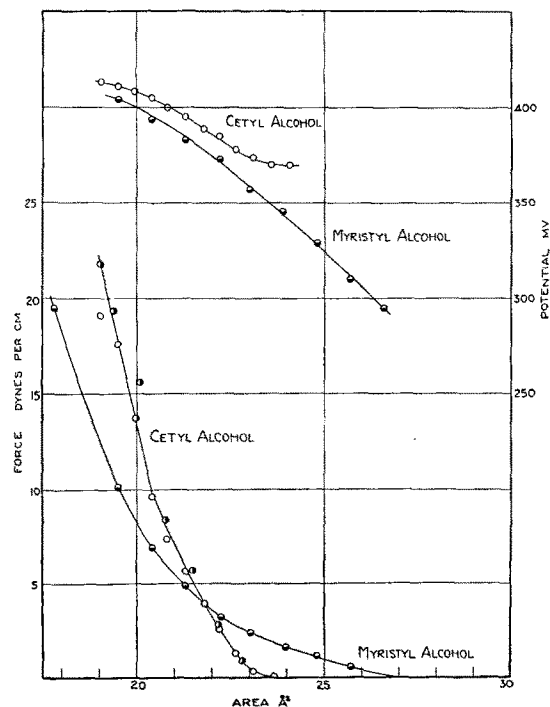

Fig. 7. Surface potentials (above) and surface pressures (below) for films of normal alcohols. As with acids the potential increases with the length of the carbon chain. Temperature, 17°.

sure exerted on the float was of the order of one dyne per cm. The film of paraffin was visible to the eye.

VIII. Surface Potentials, Dipole Moments, and the Orientation of Molecules in Surfaces

The surface potential of a film, defined as the contact potential of the surface covered by the film minus that of the clean surface of the underlying phase, is undoubtedly related to the dipole moments of the film producing substance, to the extent of the orientation of the molecules, and to other factors, some of which are geometric.

The orientation of the molecules in a surface was supposed by Hardy[15] to be due to the unsymmetrical field of the molecules, and Harkins, Davies and Clark[16] took a somewhat similar view when they assumed that the potential differences at surfaces, as well as the other energy relations may be explained on the basis of the polar setting of molecules in surfaces. An addition to this electrical theory of surfaces was made by Harkins and King[17] who consider especially the relations between surface energy, cohesion, and the polarity of the molecules which constitute the legends or liquids involved.

In a monomolecular film on water, on any other liquid, or on a solid, the molecules in the film, and to some extent the adjacent molecules of the surface region, orient themselves in such a way as to decrease the free surface energy.

In this discussion it will be assumed that just as a stone in a position above the surface of the earth possesses an energy of position, usually designated as its potential energy, a molecule in the surface possesses an energy of position which will also be termed its potential energy. The potential energy of the weight may be referred to an arbitrary zero position at the level of the earth's surface, while that of the molecule is referred to a position in the liquid phase underneath the surface region. The work done in lifting the weight is done against the force of gravitation, while that of lifting the molecule is opposed by the cohe-

[15] Hardy, Proc. Roy. Soc. **A86**, 634 (1911–12).

[16] Harkins, Davies and Clark, J. Am. Chem. Soc. **39**, 541 (1917).

[17] Harkins and King, J. Am. Chem. Soc. **41**, 970 (1919).

sional forces which may also be considered as the resultant of the electrical forces.

The potential energy of the stone with reference to its zero position, may be determined by lifting the stone, initially at rest, to the specified position. The potential energy is said to be equal to the work done. If the stone, when at the level of the earth's surface, had a velocity in the upward direction, then the work done would be less, but the final energy of position at a specified height would not be changed.

A molecule inside the liquid can in general move into the surface region only when its energy of position, which we will here call its potential energy, is supplied in the form of work, heat, or of some other class of energy.

The total energy necessary to form one sq. cm of surface is supplied partly as work γ and partly from the kinetic energy of the molecules themselves. The molecular kinetic energy is the source of almost the whole latent heat l of the surface. Thus a surface has a lower temperature than the liquid when it is first formed.

The value of the heat function h for unit area of a surface is given by the relation

$$h = \gamma + l. \tag{1}$$

In an isothermal change h is the total amount of energy which must be added to the system when a unit area of surface is created, and is usually designated as the total surface energy.

It will be assumed, on the basis of our general knowledge of surface energy relations that π, the sum of the potential energies of all of the molecules in 1 sq. cm of the surface region is very nearly equal to h the energy supplied to form unit area of the surface, or

$$\pi = h. \tag{2}$$

The orientation of the molecules causes a decrease in the free energy (γ) of the surface, while on the whole the latent heat is not greatly changed, so the total surface energy h is decreased by the orientation. Thus the sum (π) of the potential energies of the surface molecules is also decreased (Eq. (2)) by the orientation below that for a random distribution. Since the potential energy of the molecules in the surface is assumed to be due to electrical forces, it may be called the total electrical energy.

The mutual energy due to the interaction of the dipole moments of the molecules constitutes only a part of this electrical energy. In the older theory the remainder of this energy is attributed to quadrapoles or multipoles but more recently the theory has been modified by the introduction of some of the principles of quantum mechanics, as, for example in papers by Lennard-Jones.[18]

While thermodynamics predicts only the decrease of free surface energy as associated with the molecular orientation, the above discussion seems to indicate that this is in general accompanied by a decrease in the total electrical surface energy. While it is not from these relations certain that the electrical energy of the dipoles must decrease with the decrease of total electrical energy, the dipoles make an important contribution to this energy, so it seems probable that such a decrease occurs. Also from the known behavior of large scale dipoles which are free to change their orientation and position it may be deduced that the molecular dipoles will shift and orient themselves in such a way as to decrease their mutual electrostatic energy. However, the decrease may not be to a minimum since it is possible that there may be in some cases a resultant increase of the energy of the multipoles. The dipoles involved include those of the liquid (usually water) as well as those of the organic molecules of the film.

The potential difference (ΔV) between two parallel plane metal plates of an ordinary parallel plate condenser, *with a unit dielectric constant, is*

$$\Delta V = 4\pi\sigma s, \tag{3}$$

in which σ is the surface density of the charge and s is the distance between the plates.

Since $\sigma = ne$, where n is the number of electronic charges per sq. cm and e is the electronic charge,

$$V = 4\pi n(es) = 4\pi n\overline{m}, \tag{4}$$

in which $\overline{m}$ is the product of the value of the electronic charge by the distance between the plates.

Schulman and Rideal[19] consider that this equa-

tion, which they attribute to Helmholtz, may be applied to calculate the dipole moment of the molecules of the film on the basis that $\mu_s = \overline{m}$ if n is considered as the number of molecules in one sq. cm of film. Thus

$$\mu_S = \Delta V / 4\pi n. \tag{5}$$

They find, however, that the value thus obtained is only about one-sixth, or even less, of that determined by the standard methods. Their explanation of the discrepancy may be found in their papers.

Our point of view is different in that we consider that the equation of the parallel plate condenser is not valid for the case of a film.

(1) The equation assumes that the charges are on metal plates, which is far from true, since they are assumed to be associated with the molecules.

The correct equation for parallel plates of an insulating material is

$$\Delta V = 2\pi n\overline{m}'. \tag{6}$$

If now it is assumed that $\mu_s = \overline{m}'$, then the value of μ_s thus obtained is, obviously, much closer to the standard value of the dipole moment. However, this does not show that Eq. (6) is suited to the calculation of the dipole moment.

(2) The Eqs. (5) or (6) were developed for a large scale condenser. There is no evidence that they are valid for a condenser in which the charges are attached to molecules, and are a distance apart which is of the atomic scale.

(4) The charges of this atomic scale condenser are only imaginary or apparent charges, though the dipole moment is real.

(5) Even if these charges are assumed to be real and to have a definite position, the charges would move with the heat vibrations of the molecules in such a way that any instant both positive and negative charges would probably be on both sides of a plane which represents the height of the mean position of all of the imaginary charges, both positive and negative. Even if this is not the case the charges do not lie in a plane.

(6) Both the molecules and the positions of the imaginary charges are in rapid motion, which is not taken into account in the development of the equation.

Thus μ_s does not seem to be a dipole moment, but is a quantity which may be found useful,

[18] Lennard-Jones, Proc. Phys. Soc. (London) 43, 461 (1931).

[19] Schulman and Rideal, Proc. Roy. Soc. A130, 260 (1931).

since it is equal to the surface potential divided by the number of molecules in unit area of the film and this quotient multiplied by the constant $1/(4\pi)$. It seems preferable to make the constant unity. This gives

$$m = \Delta V/n. \qquad (7)$$

Either m or μ_s is thus related in a simple way to the surface potential and the concentration of the molecules in the film, and in a complicated and unknown way to the standard dipole moment. The values of m are given in Table I.

TABLE I. *Values of $m = V/n$ for films of fatty acids and alcohols, as calculated from surface potentials.*

Substrate = 0.01 N HCl (for the lauric acid films this was nearly saturated with NaCl to reduce the solubility of the lauric acid).

Compound	$m \times 10^{18}$ volts molecule^{-1} cm^{-2} at area					
	20	25	30	40	48	Sq. Å
Lauric acid	1.9	2.0	2.0	2.2$_6$		
Myristic acid	2.2$_6$	2.3	2.3	2.3	2.4	
Pentadecylic acid	2.4	2.6	2.5$_4$	2.3		
Palmitic acid	2.5$_4$	2.9$_4$				
Stearic acid	2.7	3.3				
Oleic acid	1.6$_5$	2.0	2.1$_6$	2.2	2.2$_5$	
Myristyl alcohol	2.6$_6$	2.7				
Cetyl alcohol	2.9					

In the determination of the factors which are of the most importance in their effect on the surface potential, the variation of this potential with temperature is of prime importance. In the experimental work the surface potential was found to usually exhibit a decrease with rising temperature, but a rise in temperature often changed the state of the film. The effect of increase of temperature on the surface potential of condensed films will be studied more carefully later.

IX. GENERAL DISCUSSION

There are certain features of the potential-area curves which are of importance. There is no indication in these curves of the numerous "surface phases," such as the "homalic" and "prehomalic" phases of Schulman and Rideal. Since these "phases" are not indicated by any known force-area determinations it is evident that there is no evidence that such phases have any existence, especially since both Adam and Schulman and

Hughes have also failed to find them. Doubt is also thrown upon the value of the consideration of condensed and expanded films, as defined by Adam, as distinct phases. If films in general, after being compressed to a molecular area of about 20 sq. Å, are subjected to a constantly reducing pressure, it is found that there is considerable hysteresis, both with respect to pressure and potential. With increasing pressure there is in general no special variation in the curvature of the potential-area curve at the point where the force-area curve indicates what has been considered to be the transition point between expanded and condensed phases. This fact seems to indicate that there is no sharp change in orientation or structure in the film at this point. The above considerations do not show that the terms "condensed" and "expanded" with reference to films should be abandoned, but they indicate that there is a need for a more detailed study of the reversibility of the supposed transition between the two states.

As has been stated earlier the curves for the potential-area variations as given in this paper, represent individual sets of determinations. These have been checked by numerous sets which have not been reported. The curves presented are not the smoothest which were obtained, but they were taken from several sets in good agreement with each other. The curves exhibited by Adam and Harding, and by Schulman and Hughes, in recent papers are in general either averaged or idealized, so that no specific data are presented. In some cases the same substances were used by Adam and Harding and in the present investigation, with no apparent disagreement in the results. However, since our temperatures were higher the potentials obtained are lower.

The specific experiments on films of organic acids, as presented in Fig. 6, exhibit several features of general interest. For example the surface potential for films of stearic acid at areas greater than 27.5 sq. Å may be as high as those given by the curve, or lower values may be found. However, in this individual set of determinations the potential-area curve gives no indication of any transition whatever. The same is true of pentadecylic films above 40 sq. Å. Of the two condensed films that of stearic acid is much more

coherent than that of pentadecylic acid. With such highly coherent films as that of stearic acid the surface potential is lowered only slightly as the pressure on the film is reduced. Thus it appears that the molecular orientation in such a portion of a solid film is not materially affected by the release of pressure on the film to almost a zero value. If time is given for a two dimensional evaporation of the film substance, at extremely low pressure, the surface potential is reduced to a few millivolts.

The surface potential is found to vary with

1. the length and shape of the hydrocarbon part of the organic molecule,
2. the nature and number and position of the polar groups in the molecule,
3. the hydrogen ion concentration of the solution,
4. the temperature,
5. the concentration of the film forming substance in the film,
6. the nature of any ions of salts present in the solution,
7. time, including phenomena of hysteresis.

With changes of acid concentration between 0.01 and 0.1 N the surface potentials for films of acids and alcohols was found to be only slightly affected.

The effect of hydrogen ion concentration may be illustrated by experiments on polymers of hydroxydecanoic acid with molecular weights from 208 to 16,900 and general formula $HO[(CH_2)_9COO]_xH$. A change from 0.01 normal hydrochloric acid to the same concentration of sodium hydroxide increased the molecular area in the condensed film by about 30 percent and decreased the surface potential by ten to twenty percent. Proteins were even more largely affected by the hydrogen ion concentration, as corresponds with the work of Gorter. The details of the effects of hydrogen ion concentration upon the areas and surface potentials of organic substances of high molecular weight will be left to another paper.

In order to test the assumption presented in Section I of this paper, that the method used in this work is suitable for the determination of either the surface potentials of solutions or the contact potentials of metals, the carefully cleaned surfaces of several metals were substituted for the liquid surface. The differences in these values were found to give the contact potentials of the metals as accurately as they are known for like conditions. It is obvious that the calomel cell is eliminated from the circuit for such a measurement.