

Rough measurements indicate that the vertical component of the dipole moment of the carboxyl group in the surface is somewhat diminished in the vapour state, indicating some re-orientation of the end group.

It is shown that the observed vertical components of the dipole moment are compatible with existing data on the various component dipoles of the carboxyl group.

On the Surface Potentials of Unimolecular Films. Part IV.—The Effect of the Underlying Solution and Transition Phenomena in the Film.

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INTRODUCTION.

In previous papers of this series (1) it was shown that the method of surface potentials could be developed to give quantitative measurements of the physico-chemical properties of unimolecular films at an air liquid interface.

Several problems of fundamental importance arise when a closer investigation is made of the true meaning of the phrase "surface potential of a unimolecular film."

In this work a study has been made of the phenomena attached to the deposition of a film on aqueous solutions, with special reference to the mutual influence of the solution and the polar head-group of the film-forming material.

This was considered necessary as a prelude to the general application of the method of surface potentials to the study of surface reactions and systems of biological importance. Work of this nature is in progress, and it is hoped will form the subject of a future communication.

It had already been noticed in Part III for the fatty acids that the graph of the surface potential (ΔV) against the number of molecules per square centimetre (n) showed a parallel displacement on alteration of the pH of the underlying solution over certain ranges where the state of the film remained constant. The relation of this movement to the ionisation of the head groups of the film was discussed, but it was now thought advisable to carry out the

experiments over much larger ranges of p_{H} , and to extend them to polar head groups other than the carboxyl.

EXPERIMENTAL.

The apparatus used was essentially the same as that already described in Part I,* with the addition of an arm moving on a horizontal plate holding the polonium-coated air electrode, so constructed that it moved at the required constant height over the whole of the liquid surface. This modification was found essential when investigating the homogeneity of the film.

The weak link in the accuracy of this type of work is the estimation of the area per molecule occupied by the film-forming substance. The procedure hitherto employed involves the use of a small pipette to place on the surface two or three drops of a solution of a known weight of the substance in a known weight of petrol ether. The weight of a large number, say 50, of the drops is measured; hence the weight of one drop and the weight of the substance on the surface. This method is liable to grave errors, due to the rapid evaporation of the petrol ether, and to the assumption of the uniformity of the drop size. The error in using only one drop of a calibrated solution may be as much as 10 per cent. off the mean value of 50 drops. In the earlier work no allowance was made for this error.

A new instrument was therefore devised to give molecular areas reproducible to 1 per cent. It is a micro-pipette consisting of a long fine capillary tube, calibrated for volume by a mercury thread, and fixed in a protecting glass tube. The petrol ether solution is drawn up to a definite mark on a scale placed along the capillary, by rotation of a piston fitting tightly into a rubber gland in the widened end of the capillary tube. The requisite approximate number of drops is then expelled on to the surface, but the *volume* of solution lost can be found accurately from the calibration of the capillary. The actual size of each drop is thus immaterial.

Dr. R. J. Fosbinder, of the Cancer Research Institute, Philadelphia, very kindly pointed out to us that there was an instrument on the market which could be adapted for accurate measurements of these small volumes. This is the Agla Micrometer Syringe (Burroughs, Wellcome & Co., Ltd.), which was recalibrated, and found to give consistent results to 1 per cent. on the area per molecule.

It is relevant to observe here that three different types of apparatus have been used, and they have given results for the surface potentials identical to within

* Schulman and Rideal, 'Proc. Roy. Soc.,' A, vol. 130, p. 259 (1931).

1 mv., while the results are also unaltered by the use of many different ionisation electrodes of various shapes and strengths, together with use of either silver, silver chloride or calomel reversible electrodes for the underlying solutions.

MYRISTIC ACID AND DODECYL-ALCOHOL. THE EXPANDED STATE.

It was shown in Part III* that over the region of ionisation p_H 4– p_H 6.5, the films of palmitic acid existed in the liquid condensed state, and that the value of the electric moment per molecule ($\bar{\mu}$) calculated from the slope of the curve remained constant for that state in spite of a considerable change in the value of ΔV at any given area per molecule.

On further increase in ionisation the state and slope of the curve changed, but $\bar{\mu}$ again remained constant over a range p_H 6.5– p_H 8 in the solid condensed state, the values in the two states being $1.56 \cdot 10^{-19}$ e.s.u. and $3.2 \cdot 10^{-19}$ e.s.u. respectively.

As will be seen from figs. 1 and 2, the same general behaviour is shown by myristic acid and by dodecyl alcohol for the expanded state. Myristic acid gives a series of parallel lines from N HCl to distilled water, with $\bar{\mu} \doteq 2.5 \cdot 10^{-19}$ e.s.u., while for dodecyl alcohol the expanded state continues to the most alkaline solutions studied (N.NaOH). In the case of dodecyl alcohol, the values of "n" and hence of the slope of the curve are untrustworthy, especially on alkaline solutions, owing to the solubility of the film. Thus the films can be compressed to apparent areas per molecule much less than the limiting area of 18.5 sq. A. per molecule for vertically oriented molecules. The more quickly the readings are taken after the deposition of the film, the nearer to 18.5 sq. A. is the observed area at which the film collapses.

The value of $\bar{\mu}$ in the expanded state for dodecyl alcohol is approximately $2.0 \cdot 10^{-19}$ e.s.u.

The next point of interest to be observed from the figures is the general contraction of the film as the alkalinity is increased. Thus the limiting area of the transition of the expanded state to the vapour state for myristic acid, fig. 1, " α ," changes from 55.0 sq. A. on 4 N HCl to 33.0 sq. A. on water, although on N/10 and N/100 HCl the area is the same, viz., 45.0 sq. A., the curves on these two solutions being identical. For the alcohol on 4 N HCl the expansion is so marked that a "vapour expanded" film (curve A) appears to be formed, the film remaining homogeneous up to at least 400 sq. A. per

* Schulman and Rideal, *loc. cit.*

molecule at about 20 mv. On the alkaline side, however, though the acid shows a transition to a solid condensed film at p_H values greater than 7, and ultimately forms soap films where the value of ΔV is reversed in sign, the alcohol films show no change from N/100 HCl till a pH of about 10 or 11, being still in the expanded state.

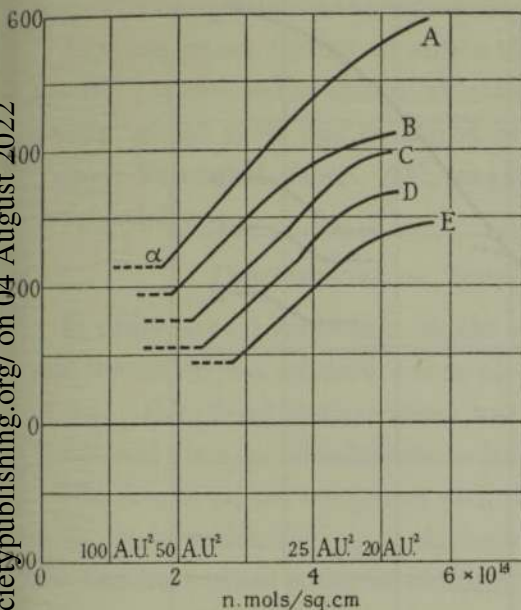


FIG. 1.—Myristic Acid, 15° C.

- A.—4 N HCl.
- B.—1 N HCl.
- C.— 10^{-2} and 10^{-1} N HCl.
- D.— 10^{-4} N HCl.
- E.—Distilled water.

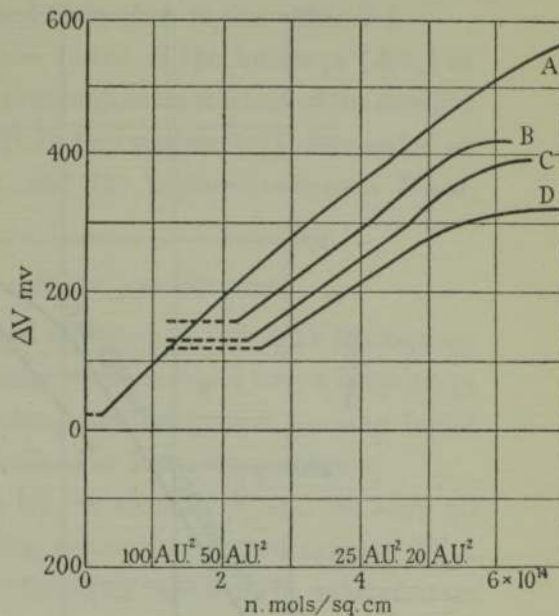


FIG. 2.—Dodecyl Alcohol.

- A.—4 N HCl.
- B.—1 N HCl.
- C.—0.01 N HCl and 0.001 N NaOH.
- D.—0.1 N NaOH.

With reference to the vapour expanded films a curve is included for comparison, showing the behaviour of ethyl myristate on N/100 HCl, fig. 3. Here the film remains homogeneous down to the lowest measurable surface potentials, at areas larger than 500 \AA^2 per mol, in direct contrast to the "expanded" films which break down to inhomogeneous two-phase systems.

Vapour expanded films, as shown by N. K. Adam, are expanded films above the critical temperature.

TETRADECYL ALCOHOL.

Tetradecyl alcohol at 32° C. forms an expanded film which shows an essentially similar behaviour to that of dodecyl alcohol at room temperatures, but accurate results are again not possible owing to the solubility of the film.

It is interesting to note, however, that tetradecyl alcohol, fig. 3, which gives liquid condensed films at room temperatures from N HCl to N NaOH, gives on 4N HCl an expanded film with a limiting area at 55 sq. A. per molecule, again indicating the very marked effect of concentrated hydrochloric acid in expanding the film, as was observed on dodecyl alcohol.

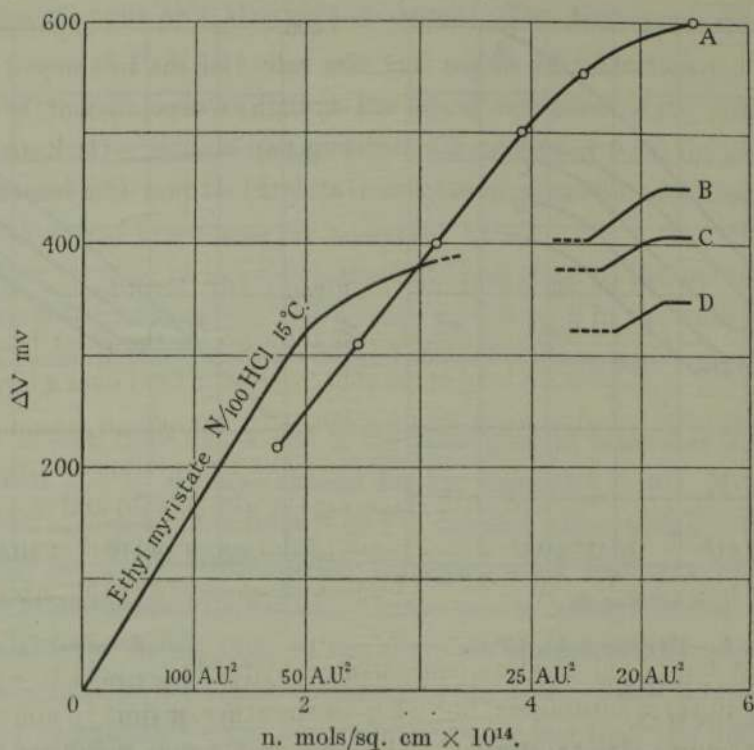


FIG. 3.

The effect of p_H on films of the alcohols is again reflected in the condensed films of tetradecyl alcohol, which show the same behaviour from N/100 HCl to p_H 10 or 11, but contract both in area and potential at higher p_H values. The slope of these lines is constant, and gives $\bar{\mu} = 1.1 \cdot 10^{-19}$ e.s.u. The condensed films of alcohols will be discussed in detail later.

For the liquid condensed films of palmitic acid a similar expansion has been noticed on increasing the acidity of the underlying solution (Part III) (*loc. cit.*), as also observed in the force/area curves by Lyons and Rideal.*

Beyond the superior limiting areas of the expanded state the films become inhomogeneous, the value of ΔV showing large fluctuations over the surface. Below the limiting area the linear character of the $\Delta V/n$ curves is preserved down to areas of about 35–30 sq. A. per molecule, but at this point transition

* 'Proc. Roy. Soc.,' A, vol. 124, p. 322 (1929).

to the liquid condensed state begins. From 35–25 sq. A. per mol down to about 25 sq. A., the curve does not seem to be definitely reproducible, and fluctuations in potential can sometimes be detected over the surface, of about 20–30 mv., though this is dependent on the rate of compression of the film. By about 25 sq. A., however, the slope of the curve has decreased markedly and is much smaller in the liquid condensed state than in the expanded.

It is important further to notice that the values of the intercept (ΔV_u) of the $\Delta V/n$ curves on the axis of ΔV obtained through extrapolation of the straight portion of the curve can be placed broadly in two classes:—(1) Expanded or Vapour-Expanded Films, ΔV_u negative, and (2) Liquid Condensed Films, ΔV_u positive.

COMPARISONS OF ACIDS, ALCOHOLS AND ETHERS.

In order to cast more light on the mutual influence of the polar head-group and the underlying solution, a long-chain ether was examined over a large range of p_H . Octadecyl methyl ether was chosen, this compound forming liquid condensed films on all solutions so far examined at room temperatures.

The results (a) are compared with those for the alcohols (b) and the acids (c) in fig. 4, in which the p_H of the underlying solution is plotted against ΔV_∞ , the limiting surface potential obtained by placing an excess of the substance on the surface.

The sharp rise of potential on concentrated hydrochloric acid is seen to be common to all three substances, but whereas the ether, definitely non-acidic in character, acquires almost identical values for the surface potential at p_H 2 as at p_H 12 (453 mv. and 448 mv. respectively), the alcohol shows a marked falling off at p_H 12 and at greater p_H values.

The behaviour of the acid is very definite, ionisation of the film setting in between p_H 3 and 4, with a complete reversal of sign beyond p_H 9.

It was noticed in the case of the alcohols on alkaline solutions that the initial value of ΔV was always some 30–40 mv. higher than the final equilibrium value, the fall taking place in about three minutes. It is possible that this represents the actual course of ionisation or partial ionisation of the OH group, the value of ca. 400 mv. from p_H 1–10 being that of the unionised alcoholic group. This effect is similar to that occurring during the ionisation of the acids.

INFLUENCE OF SALTS.

A further series of experiments was carried out to investigate the effect on the surface potential of the film of solutions containing a variety of ions.

Salts were used which both raise or lower the surface tension of water. Thus, for tetradecyl alcohol KCl had no effect at any concentration from N/100 to 3.5 N, but LiCNS, N/2, caused an increase of 25 mv.; potassium ferricyanide, sodium citrate, ethylamine hydrochloride, an increase of ca. 10 mv.; and

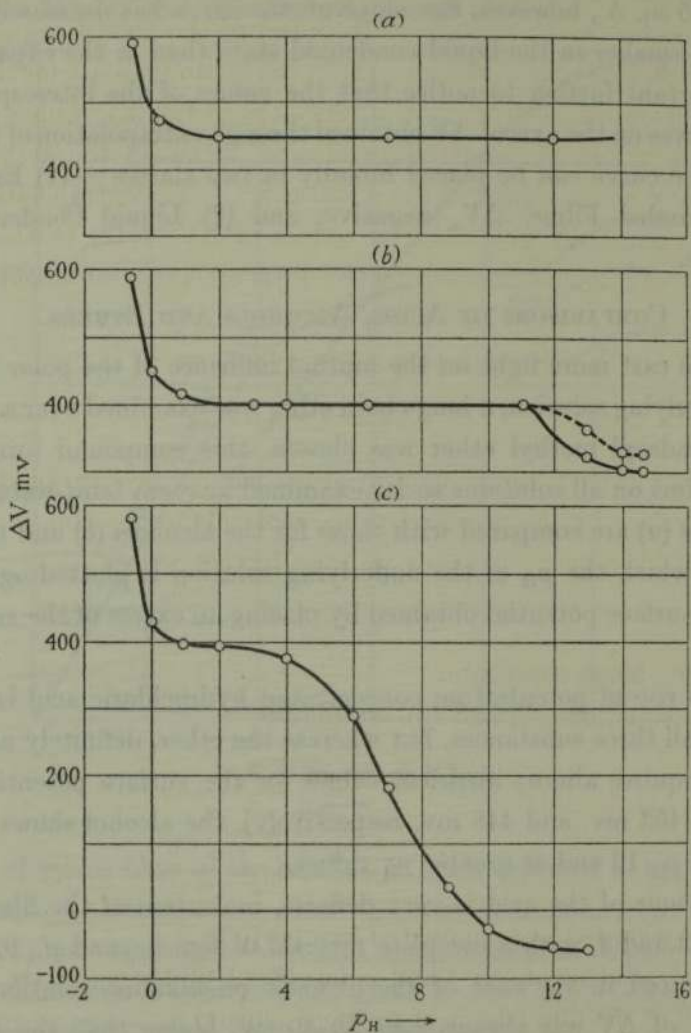


FIG. 4.

$\Delta V_{\infty} / p_{\text{H}}$ curve 15° C.

ΔV_{∞} corresponds to an area approximately 20 A^2 per mol.

a. Octadecyl methyl ether; b. tetradecyl alcohol; c. Myristic acid.

$\text{Al}_2(\text{SO}_4)_3$ — N/100 p_{H} 4.7 — an increase of ca. 35 mv., all reckoned from the value of 400 mv. on distilled water. In no case has a decrease been observed, except where it is reasonable to assume ionisation of the film. For the ether no alteration of the potential could be detected due to the nature of the ions

in the solution, the value of ΔV_z remaining constant at 448 mv. on all these solutions.

DISCUSSION OF RESULTS.

In summarising the experiments on the expanded and condensed films of the acids and alcohols, with reference to the effect of the underlying solution, the following conclusions may be drawn: (1) In the expanded state for the acids and the alcohols there is little alteration in the slope of the $\Delta V/n$ lines over a very large range of p_H of the underlying solution, although the actual value of "n" may vary to the extent of some 250 mv. The extrapolation of these lines to the axis of ΔV give negative values of ΔV_u . (2) In the condensed film of acids and alcohols, parallel straight lines are again obtained over large p_H ranges, the ΔV_u values here being positive.

We may apply the Helmholtz equation and write

$$\Delta V = 4 \pi n \mu \tag{1}$$

where μ is the total vertical component of the polypole system produced at the air liquid interface by the presence of one molecule in the film.

Where the $\Delta V/n$ graph is linear we may further write

$$\Delta V = an + b \tag{2}$$

"a" and "b" being constants.

Combining equations (1) and (2), we obtain

$$4 \pi n \mu = an + b$$

or

$$\mu = \frac{1}{4\pi} \left(a + \frac{b}{n} \right) \tag{3}$$

i.e., μ can be regarded as composed of two portions:—

(i) $a/4\pi$ independent of "n" and independent of the p_H of the solution in any one state of the film (the $\bar{\mu}$ of previous papers).

(ii) $b/4\pi n$ varying inversely as "n" and dependent on the p_H of the solution ($b = \Delta V_u$ of previous papers).

Thus (α) if "b" is positive, then, as "n" increases, μ decreases (condensed state); but

(β) if "b" is negative, as "n" increases μ increases (expanded state).

Thus the simplest interpretation of this analysis is that in any one state of the film the total μ consists of a portion $\bar{\mu}$ or $a/4\pi$, which is that of the film-forming material itself, and is constant for that state; and of a portion

$b/4\pi n$, which represents the manner in which the contribution due to the underlying solution is affected by compression of the film. As has already been noticed, the order and sign of the value of ΔV_u are characteristic of the state of the film, but too great stress must not be placed on the numerical values of ΔV_u , since these are obtained by extrapolation of the $\Delta V/n$ curves.

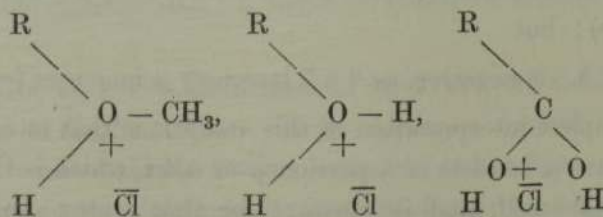
It is clear, however, that in compression of the expanded state the contribution of the underlying solution is *increasing* in the manner given by the term $b/4\pi n$ when "b" is negative.

Whether we may consider "b" as being due to an orientation of solvent molecules in the neighbourhood of the polar head, together with a resultant dipole moment, or due to preferential adsorption of the ions in the Gibbs' layer, is at present difficult to decide; the latter effect is definitely present, as shown by the effect of different salt solutions on the film potentials.

Further, on compression of the condensed state the contribution of the underlying solution is *decreasing*, since "b" is now positive. This may be ascribed either to an expulsion of oriented solvent molecules from the vicinity of the head groups when these become close packed in the condensed state, or to a marked change in the distribution of the ions in the Gibbs' layer.

Referring once more to figs. 1, 2 and 3, in regard to the effect of hydrochloric acid solutions on the film, an increase of the acid concentration above N/10 results for the acid, alcohol or ether in a gradual expansion of the range of homogeneity of the films, together with a general rise of potential. The change of $\bar{\mu}$ is, however, not large, increasing from $2.5 \cdot 10^{-19}$ e.s.u. for myristic acid in the expanded state on N/10 or N/100 HCl to $3.0 \cdot 10^{-19}$ e.s.u. on 4 N HCl; and from $1.9 \cdot 10^{-19}$ e.s.u. on N/10 or N/100 HCl to $2.1 \cdot 10^{-19}$ e.s.u. on 4 N HCl for dodecyl alcohol, also in the expanded state. For the ether the range of existence of the condensed film is so small—about 21 sq. A. to 19 sq. A.—that the slopes cannot be estimated with accuracy.

This general behaviour on solutions of hydrochloric acid may be interpreted as being due to the formation of an ionisation-complex on the polar head-group. In the extreme case one might postulate the formation of oxonium compounds of the type:—



for the ether, alcohol and acid respectively. This results in an increase of the dipole moment of the film if carried to completion, and a definite alteration both in moment and in distribution of the ions in the Gibbs' layer if the formation of this type of complex is only partial. These effects are observed. The greater the concentration of HCl in the underlying solution, the greater the change in moment. It must be emphasised that the values here obtained for the dipole moment refer only to the *vertical component* of the polypole system. It is impossible to specify the total change which may occur in the head group and its surrounding ion atmosphere.

For the ether, alcohol and the acid head group, the dissociation of the HCl complex appears to be complete when the HCl concentration in the solution has sunk to N/10. Thence onwards, with increasing p_H , the ether shows no further change in the head group or the underlying solution. For the alcohol no change is observed up to a p_H of about 10, but beyond this point ionisation sets in, and can be followed by the sharp falling off in the film potentials; and for the acid this falling off occurs at a much smaller p_H value, setting in at about p_H 4.

The general form of ionisation curve is very similar to that found in an electrometric titration in the bulk phase, fig. 4.

The behaviour of the alcohol indicates that it is acting as an acid with a dissociation constant of about 10^{-13} . It is interesting to compare this result with those obtained by Michaelis and Rona* for the acid dissociation constants of sugars, which were found to give $K_a. = 10^{-13}$.

It would be of great interest in this connection to examine the cataphoresis of these acids and alcohols over a large range of p_H , and also in the presence of different types of ions.

The work of G. Köhler† on the electric endosmose of liquid through a palmitic acid diaphragm has shown that there is no relative movement at p_H 3.6, but at greater p_H values ionisation and movement takes place. No work appears to have been carried out on the alcohols, or on the acids on more strongly acid solutions.

The results we have obtained on the general effect on the surface potential of the film due to the presence of various salts in the underlying solution, show that small changes in the values of ΔV can be effected, causing a small parallel displacement to the $\Delta V/n$ curve. For tetradecyl alcohol the changes were in no case greater than about 35 mv. (on N/100 aluminium sulphate), and

* 'Biochem. Z.,' vol. 49, p. 232 (1913).

† 'Z. phys. Chem.,' A, vol. 157, p. 134 (1931).

always in the same sense, namely, an increase in the original potential obtained on distilled water.

The sign of the potentials of these films shows that the dipole moment is positive above and negative below. It is reasonable to suppose that adsorption of ions in an oriented layer under the film will take place by electrostatic adsorption, giving a second layer positive above and negative below. This results in an increase of the observed values of ΔV .

These small variations in potential are comparable in magnitude to the values obtained for zeta potentials in cataphoretic experiments, as distinct from the order of magnitude of the changes occurring when ionisation of the film is taking place, which may amount to 200 or 300 mv.

It is clear that if there is no orientation of dissolved substances in the underlying layer, these will have no effect on the potential of the film, even though they may produce large changes when present alone at the air-liquid interface. This is exemplified by the behaviour of a long-chain methyl ether, the film potential of which is independent of the presence of a large number of substances in the underlying solution.

These considerations permit us to draw a distinction between oriented adsorption in the Gibbs' layer and actual chemical changes occurring in the film.

TRANSITIONS.

The Vapour/Expanded Transition.

A moving electrode was employed in investigating the limiting areas of the vapour/expanded transition. It was found that the films at areas beyond 45 A^2 for myristic acid on N/100 HCl were inhomogeneous. This fact was first pointed out to the authors by Adam and Harding, who, in the course of experiments on surface potentials, had found that by blowing on the surface very large fluctuations occurred in the potentials over this range. As an apparatus had already been constructed with a movable electrode for investigating the limiting area of the condensed states, where large fluctuations had already been noticed (Part III), the observation of Dr. Adam was soon confirmed.

In Part I the polonium source was fixed stationary over that end of the trough towards which the film was compressed, and inhomogeneity was only noticed at areas greater than about 100 A^2 per mol. This was found to be due to the expanded form of the myristic acid existing in large islands, which on compression collected under the polonium electrode long before the surface was

homogeneous. These islands had a maximum potential of 152 mv., and the vapour film existing between them possessed a very low surface potential of approximately 2 mv.

Since the surface pressure remains constant over this region and the potentials of the two forms of the film present are so very different, the limiting area of the phase with the larger surface potential was easy to determine with accuracy.

The limiting area of the vapour film, on account of its very small surface potential, was much more difficult to determine. The method employed was to observe the area at which the islands of the expanded film disappeared and the whole surface became a homogeneous vapour film. The polonium was moved systematically over the surface, and all non-uniformities with their potentials were localised. These islands were then closely observed over a contraction and expansion of the film.

It appeared at first that the surface became uniform with a potential of about 2 mv. at areas of 300 A², and the curves seemed consistent with those already published (Part I). But on closer observation it was found that there was considerable non-uniformity of about 10–20 mv. within 1–2 cm. of the edges of the trough. It may be added that the uniformity of the potential of the liquid surface was examined in the absence of the film and found to be uniform within 2 mv. even up to a few millimetres from the edges of the trough.

That the liquid portion of the film in the transition region should tend to collect along the edges of the trough was apparently due to the spreading of the petrol ether solution. It was noticed in a blind experiment using pure petrol ether alone, that any surface contamination was swept to the edges of the trough by the petrol ether. This was a convenient and sensitive method of checking the purity of the surface.

Non-uniformities were quite definitely present on the surface from areas of 700 A² per mol. to 45.5 A² at 15° C. At areas of 1000 A² per mol. changes of only 1–2 mv. from the zero value were noticed over the whole surface. Assuming that the surface is uniform at 45 A² per mol. at a potential of 152 mv., one may calculate the fraction of the total surface at any larger mean area per molecule which should be covered with the 152 mv. species of film, if the latter is unchanged on expansion. This may be compared experimentally with the area so covered, as found by moving the polonium electrode over the surface. The values so observed were always well below the calculated value for areas beyond 100 A².

The explanation of this is probably that the islands of the 152 mv. expanded film are becoming too small to occupy the area subtended by the whole solid angle of the ionisation region of the polonium source.

In summarising, one may say that the range of inhomogeneity agrees very well with the limits of the transition already found by Adam and Jessop* for the myristic acid vapour/expanded transition, namely, from $850 \text{ \AA}^2 - 48 \text{ \AA}^2$ per mol. at 16° C . This inhomogeneity of the transition shows there is no necessity for assuming the pre-Homalic state (*cf.* Part I).

The low values of ΔV for the vapour state at 850 \AA^2 may be compared with the values for the vapour films of soluble substances. Thus, butyric acid gives a ΔV of 22.5 mv. when " n " deduced from the surface tension depression is $0.35 \cdot 10^{-14}$ mols./sq. cm., corresponding to an area per molecule of about 300 \AA^2 per mol. The vapour expanded films of dodecyl alcohol on concentrated HCl and of ethyl myristate on N/100 HCl give the same order of ΔV (20 mv.) at these large areas.

The moving air electrode permits of an interesting experiment in that one can follow the surface solution of a crystal of, say, myristic acid placed in the liquid surface.

In Part I, curves were shown of the change of surface potential with time at a fixed point on the surface during the process of surface solution. When a large island of the expanded state (with a potential of 152 mv.) arrived under the polonium electrode the surface potential remains constant until the end of the transition, when the whole of the surface is covered with this form. Then the pressure increases and the potential rises proportionately until the equilibrium spreading pressure is reached.

If the polonium electrode is placed next to the crystal immediately it has been placed in the surface, violent fluctuations of potential (0–100 mv.) take place within 1–2 cm. of the crystal. Beyond this point there is a region of uniform potential at 152 mv. in the form of a gradually expanding wave with a sharp boundary. In front of this there is a potential of only 1–2 mv., *i.e.*, the vapour film.

The rate of spreading of the 152 mv. form (the uncompressed expanded film) can be readily followed with the moving electrode. This method of following the spreading of films could be made of general application.

The fluctuations of potential in the immediate vicinity of the crystal were explained by observations with a dark-field ultramicroscope of the type

* 'Proc. Roy. Soc.,' A, vol. 110, p. 423 (1926).

designed by Zocher and Stiebel.* Here concentric rings of minute crystallites, similar to those appearing in the "point structure," at film collapse, were seen to spread off from the surface of the crystal and dissolve away within a few millimetres.

The Expanded/Condensed Transition.

The moving electrode was again of use in observing the transition of the film from the expanded into the condensed state. On compression of a film of myristic acid on N/100 HCl to areas smaller than about 35 A² per mol., the potentials begin to show fluctuations over the surface to the extent of some 20 mv.

The film becomes uniform again at smaller areas, below about 27 A² per mol., and on expansion the process is reversible.

These fluctuations do not always occur. Thus, on depositing the film on the surface directly at an area of about 30 A² per mol., the film is uniform and the potential follows the repeatable course shown in fig. 1. The fluctuations appear, however, when the film is compressed from larger areas. Whether the non-uniformity really indicates the presence of two distinct phases, liquid expanded and liquid condensed, or whether it is due to local collapse of the film, is difficult to decide. From the measurements of surface pressures (N. K. Adam†), a definite break in the Force/Area curves is always found at areas of about 35 A² per mol. at 15° C.

At smaller areas than about 30 A² a gradual change in the slope of the $\Delta V/n$ curve occurs, and the value of $\bar{\mu}$ decreases, the final portion of the curve corresponding closely with that of the liquid condensed films of palmitic acid under the same conditions.

It is worthy of note that myristic acid at 5° C. gives a curve at slightly higher values for ΔV following the upper portion of that obtained at room temperature, the limiting area now being 28 A²; the change of slope ($\bar{\mu}$) is also noticed as the film becomes condensed. There is thus a marked change in the character of the film, as shown by the surface potentials as well as by the surface pressures.

THE VAPOUR/CONDENSED TRANSITION.

Transitions in the Condensed State.

In Part III, and in the present work, reference has been made to the condensed films of palmitic acid and of tetradecyl alcohol. Further experiments

* 'Z. phys. Chem.,' A, vol. 147, p. 401 (1930).

† "The Physics and Chemistry of Surfaces," chap. 2, London (1930.)

on this type of film have been made with hexadecyl and eicosyl alcohols to examine the influence of the nature of the polar head and of the chain-length on the general behaviour in the condensed state.

The range of existence of the condensed state is relatively small—at the most from about 23 \AA^2 to 18.5 \AA^2 per molecule in these cases—and the limiting factor in the accuracy of these experiments is the estimation of the molecular areas. These can be measured to 1 per cent.

The Force/Area curves for hexadecyl and eicosyl alcohols were determined for comparison of the limiting areas of the condensed state obtained in this way with those obtained by the method of surface potentials.

FORCE/AREA CURVES.

Fig. 5 shows the behaviour of hexadecyl alcohol on N/100 HCl at room temperature, and is typical of the condensed state, the graph being clearly

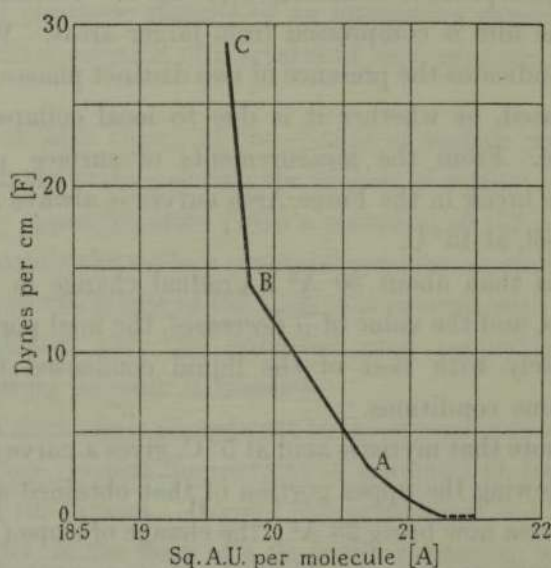


FIG. 5.—Force/Area Curve. Hexadecyl alcohol N/100 HCl 15°C .

divided into two straight lines, AB and BC, representing a high and a low compressibility respectively. The film is liquid even up to the highest compressions, a point of some interest to which reference will be made later.

Fig. 6 gives the Force/Area curves of eicosyl alcohol also on N/100 HCl. At low temperatures this alcohol forms a definitely solid film, and its behaviour was, therefore, examined over a range of temperatures from 4°C . to 31°C ., with a view to correlating the phase change in the film, as observed by the

motion of talc particles placed on the surface, with any change in the form of the force/area curves.

At 4° C. the film is solid, and a noticeable surface pressure is first obtained at an area of 21.0 A² per mol., and a linear increase in pressure is obtained down to 19.1 A² per mol. in the AB form of high compressibility. The form of low compressibility and high pressures is unstable at this temperature, and the film readily collapses above 10 dynes per cm.

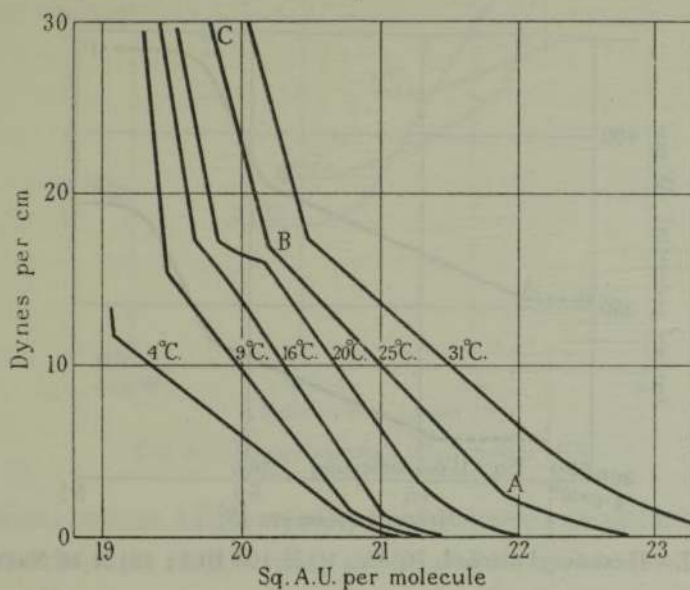


FIG. 6.—Force/Area Curves. Eicosyl alcohol [C₂₀] N/100 HCl.

Up to 16° C. the same type of curve is obtained as on hexadecyl alcohol, and the second portion, BC, can be followed from the change point B, at 17 dynes per cm. to pressures above 30 dynes per cm. The AB film is now liquid and the BC film solid.

In the neighbourhood of 20° C. the force/area curves show a peculiar arrest level from 20.1–19.8 A² per mol. just before the steep rise in pressure along BC. Above 22° C. the film is liquid throughout, and gives the usual type of curve. There is no sharp melting point of the film. A gradual increase of the molecular areas with rising temperatures is obtained of about 10 per cent. for a range of 27 degrees. The results of Adam and Dyer* on the alcohols appear to agree with the results here given at room temperature.

SURFACE POTENTIAL CURVES.

The surface potentials (ΔV) in the condensed films show a similar change of form, at a definite area per molecule, as the force/area curves, and provide more

* 'Proc. Roy. Soc.,' A, vol. 106, p. 694 (1924).

detailed information as to the nature of the film. In the case of hexadecyl alcohol, the effect of the underlying solution, and in the case of eicosyl alcohol the effect of alteration of temperature, has been investigated. The values of ΔV are plotted as usual against " n ," the number of molecules per sq. cm., instead of " A ," the area per molecule, since the slope of the $\Delta V/n$ curve gives information as to the dipole moment of the molecule. The results on hexadecyl alcohol are given in fig. 7.

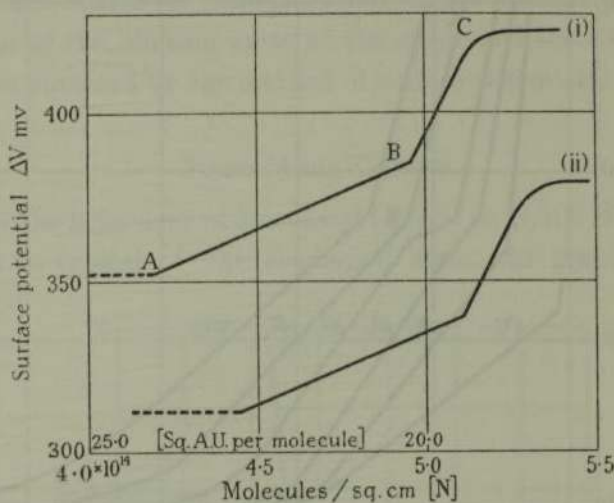


FIG. 7.—Hexadecyl alcohol, 16° C. (i) N/100 HCl; (ii) N/10 NaOH.

At areas larger than about 23 Å^2 per mol. the film is inhomogeneous, the potentials fluctuating from 50–350 mv. in an irregular manner. This is due to the presence of large islands of condensed film in equilibrium with a vapour film of the alcohol. This vapour film has a very small two-dimensional vapour pressure, and a very small surface potential, as found for the vapour of myristic acid.

On compression of the film below about 22 Å^2 per mol., a slow uniform rise of potential is obtained, but at a definite point B the potential rises suddenly and steeply till the film collapses. This change point agrees within experimental error with the point B on the force/area curve, at $20.0 \pm 0.1 \text{ Å}^2$ per mol.

As in the case of the lower alcohols, the curves on N/10 NaOH are some 50 mv. lower in potential than on N/100 HCl, but the form of the curve is similar. The film appears to be slightly contracted on a strongly alkaline solution; on careful compression an area per molecule as low as 18.6 Å^2 may be obtained before the film collapses, the whole curve being slightly displaced to the right as compared with that on the acid solution.

Fig. 8 gives the results for eicosyl alcohol. At the lowest temperature the high potential form is not obtained, owing to film collapse, but it appears as a stable form on raising the temperature in exactly the same manner as the high pressure form on the force/area curves (of fig. 6). At temperatures of about

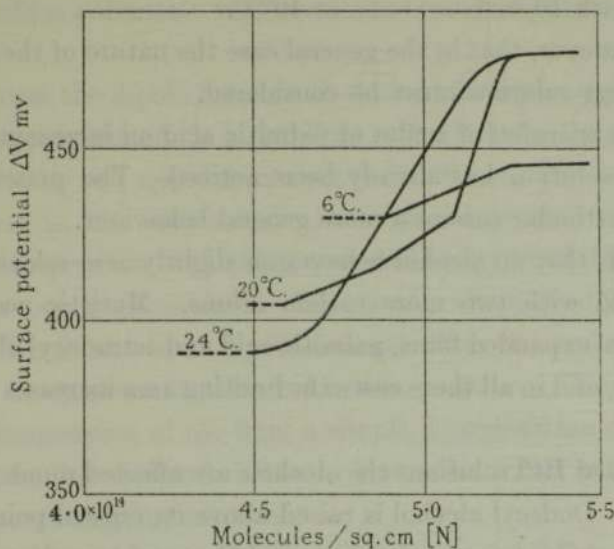


FIG. 8.—Eicosyl alcohol [C₂₀] N/100 HCl.

20° C. the initial portion AB, previously linear, shows a small kink of increasing potential over the same range of area as the arrest level obtained on the force/area curves at the same temperature. The film then passes over into the high potential form.

At higher temperatures the high potential form is obtained at still larger areas, and the same general expansion with temperature as observed on the force/area curves.

DISCUSSION.

In a general way it may be said that the values of the lateral surface pressures indicate the behaviour of the hydrocarbon chain, while the surface potentials indicate that of the polar head group, this being the seat of the predominant electrical dipole in the molecule.

It appears that four factors can operate in determining the structure of the film :—

- (i) The length of the hydrocarbon chain.
- (ii) Temperature.
- (iii) The nature of the underlying solution.
- (iv) The nature of the polar head group.

It is well known from the work of Adam (*loc. cit.*) that increasing the chain length has the same effect as decreasing the temperature; in either case the cohesion of the chains to each other is increased. Thus a film of myristic acid, with 14 carbon atoms at 20° C. behaves similarly, *ceteris paribus*, to a film of palmitic acid with 16 carbon atoms at 40° C.

It is clear, however, that in the general case the nature of the polar head and of the underlying solution must be considered.

The gradual expansion of a film of palmitic acid on increasing the acidity of the underlying solution has already been noticed. The present work shows that this is a particular case of a more general behaviour.

Thus one finds that an alcohol behaves on slightly acid solutions in a similar way to the acid with two more carbon atoms. Myristic acid and dodecyl alcohol both give expanded films, palmitic acid and tetradecyl alcohol both give condensed films, and in all these cases the limiting area increases with increasing acidity.

On concentrated HCl solutions the alcohols are affected much more markedly than the acids. Dodecyl alcohol is raised above its critical point, and changes from an expanded film to a vapour expanded film, and tetradecyl alcohol from a liquid condensed film to an expanded film, while in the case of myristic acid the film remains in the same state as an expanded film, but the limiting area is considerably increased, from 45 A² per mol. (N/100 HCl) to 55 A² per mol. (4 N HCl).

With regard to the condensed films it was at one time thought that the two branches of the typical force/area curve (*e.g.*, AB, BC, fig. 5) could be identified with a "liquid" condensed and a "solid" condensed film respectively.

This view is contradicted by the particular case in point, hexadecyl alcohol, where the condensed film is definitely liquid throughout.

As noticed by Adam (*loc. cit.*, p. 60), palmitic acid and hexadecyl alcohol, under precisely the same conditions (on water at 15° C.), give a solid condensed and a liquid condensed film respectively along BC. This shows that the head group exerts a considerable influence on the behaviour of the hydrocarbon chain for the same chain length, the same temperature and the same underlying solution.

It is thus incorrect to describe the two types of condensed film (AB, BC) as solid and liquid as a comprehensive nomenclature. They will here be designated for convenience by "α" and "β" condensed film respectively.

A second view that has been put forward to explain these two states is that the "α" form represents compression of the head-groups and the "β" form

the compression of the close-packed hydrocarbon chains. It is assumed that the polar head group occupies a larger area of surface, and is more easily compressible than the non-polar chain (Adam, *loc. cit.*). From a study of the force/area curves alone this conclusion is justifiable, but the results obtained on surface potentials indicate that a reconsideration of the case is necessary.

In the "α" form the dipole moment $\bar{\mu}$, derived from the slope of the $\Delta V/n$ curve, is small, approximately $1.1 \cdot 10^{-19}$ e.s.u. per mol. for the alcohols on acid or alkaline solutions, and approximately $1.5 \cdot 10^{-19}$ e.s.u. per mol. for the acids (Part III). That is, the moment of the head group itself is not changing appreciably on compression of the film, as would be expected if the head groups themselves were being compressed. The factor which is altering, however, is the contribution to the total dipole moment from the underlying solution, the term $b/4\pi n$ in equation (3), where b is now positive. This contribution is decreasing on compression of the film, a simple interpretation of which is that the solvent molecules oriented between the polar head groups are being expelled into the underlying solution.

On further careful compression of the film into the "β" form there is a very marked change in the $\Delta V/n$ curves, both in the case of the acids (Part III) and of the alcohols. The potential rises sharply over a very small range of area, the portion BC in fig. 7, prior to film collapse.

This change must be associated with a re-orientation of the CH_2OH or COOH groups when they are brought into close proximity. This re-orientation is assisted by a rise of temperature, occurring at larger areas as the temperature is raised.

As noted by Adam and Dyer (*loc. cit.*), as the chain length is increased the condensed films show a slightly closer packing. This observation is confirmed in this work on the alcohols. For hexadecyl alcohol at 15°C . the transition point B, between the "α" and "β" condensed states occurs at 19.8 \AA^2 ; for eicosyl alcohol this has decreased to 19.5 \AA^2 .

At the same time it must be noticed that the total potential in the condensed films is ca. 40 mv. higher in the case of eicosyl alcohol than for hexadecyl alcohol. No simple explanation of this phenomenon seems available.

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SUMMARY

(1) The effect of the underlying solution on the surface potentials of unimolecular films of long chain aliphatic compounds has been examined over a large range of p_H , and for the specific effects of various ions in the underlying solution.

(2) A distinction is drawn between ionisation of the film-forming material and adsorption of ions on the film.

(3) Two-dimensional transitions of state are discussed in detail.

The Behaviour of Electrolytes in Mixed Solvents. Part IV.—The Free Energy of Zinc Chloride in Water-Alcohol Solutions.

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In Part I of this series* were described measurements of the free energy and heat content of hydrogen chloride in a series of water-alcohol mixtures. It appeared to be very desirable to find if the behaviour shown by hydrogen chloride is typical of that of strong electrolytes in general. For this purpose an attempt was made in the first place to determine the free energies of lithium chloride in these solvents, using amalgam electrodes. Preliminary measurements showed that even under rigidly air-free conditions reproducible values of the electromotive forces of cells containing lithium amalgams could not be obtained in alcohol solutions. Similar experiences with sodium amalgams have been reported from the Balliol College Laboratory,† while Scatchard‡ has also experienced similar difficulties with calcium amalgams. It appeared that

* Butler and Robertson, 'Proc. Roy. Soc.,' A, vol. 125, p. 694 (1929).

† Wolfenden, Wright, Rose Kune, and Buckley, 'Trans. Faraday Soc.,' vol. 23, p. 491 (1927).

‡ Private communication.