179. *The Properties of Freshly-formed Surfaces. Part VIII. Expansion of Soluble Films of Decoic Acid at the Air–Water Interface.*

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The theoretical tensions operating at the surface of drops expanding at known rates have been calculated from (*a*) the surface tensions of decoic acid solutions at stationary (*i.e.*, non-expanding) surfaces recorded in Part VI (*J.*, 1946, 579) and (*b*) measurements of the volume–surface area relation for expanding drops. These calculations assume that the surface activity of an adsorbed molecule is not influenced by expansion of the surface, and the calculated values of tension are appreciably lower than those actually observed. Possible reasons for the decrease in surface activity of a soluble film during expansion of the surface are discussed. Change in orientation of the adsorbed molecules provides the most satisfactory explanation of the effect, which is common to other long-chain adsorbates.

Numerous investigations have confirmed that the surface tension of a solution depends upon the state of the surface as well as the bulk concentration of the solute, and may therefore vary with the method of measurement employed. The amount of adsorbed material in an insoluble film is known and constant, and this enables a ready interpretation of surface pressure–surface area curves to be made on the basis of state and orientation of the adsorbed layers. However, similar studies of soluble films are complicated by two factors. First, the interchange of solute between surface and bulk solution which occurs as surface area changes nullifies the variations in surface pressure which would otherwise result; for instance, Ford and Wilson (*J. Physical Chem.*, 1938, **42**, 1051), studying the compression of soluble films of phenol, β-phenylpropionic acid, and octoic acid, by a piston film of oleic acid, found that, although aged surfaces presented some resistance to the spread of oleic acid, fresh surfaces showed no such resistance. Secondly, few direct determinations of the surface excess of adsorbate have been made, and quantitative treatment of soluble films must usually rely upon the application of the Gibbs equation. The expansion or contraction of a fresh soluble film has not hitherto been considered to have any significant influence on the surface activity of the adsorbed molecules, although surface expansion is a feature common to several of the standard methods of surface tension measurement. However, the following results for decoic acid indicate that surface activity may be decreased to an appreciable extent during surface expansion, and these studies have been extended to other solutions (see Part IX, following paper) in view of the information they may provide on orientation of long-chain molecules at interfaces.

The surface tension of a solution may be influenced by surface expansion in at least two ways: the tension may rise owing to dilution of the surface layer, and it may vary with change in orientation in the film. (The term orientation is used here for simplicity, and its use does not exclude the possibility that change in position of adsorbed molecules with respect to the plane of the surface, as well as change in angle, may occur.) In most solutions of appreciable concentration, the first factor may be neglected; thus the changes in surface tension observed on expanding the surface of solutions of sodium dodecyl sulphate (Part IX) may be suitably explained by the orientation effect alone. However, such measurements provide no evidence that a given number of molecules adsorbed on unit area of a stationary (*i.e.*, non-expanding) surface produce a lowering of the tension which is different from that at an expanding surface. In this paper an attempt is made to obtain quantitative proof of this effect; this has been achieved by studying the decoic acid system, in which dilution of the surface, and change of orientation during expansion, can both influence the measured tensions. It has already been shown (Part VI, *J.*, 1946, 579) that the surface tensions as measured by the drop weight method may vary over a range of 20 dynes/cm. with rate of expansion of the drop surface.

Scheme of Calculation, and Use of the Gibbs Equation.—Adam (" Physics and Chemistry of

Surfaces ", Oxford Univ. Press, 2nd edtn., 1938, p. 118) has found striking agreement between experimental results and those calculated by using the Gibbs equation for the C_{12} carboxylic acid, and Ford and Wilson (*loc. cit.*) have obtained fairly close agreement for the C_8 acid. Therefore the equation is probably applicable with sufficient accuracy to the equilibrium tension–concentration curves for the dilute decoic acid solutions used; it is to be emphasised, however, that no conclusions given below depend upon the exact quantitative applicability of the equation, and that the equation is not applied directly to expanding surfaces. The equilibrium tensions at various concentrations reported in Part VI (*loc. cit.*) have been substituted into the approximate form of the Gibbs equation to derive a Γ–γ relation for decoic acid solutions. From a knowledge of the change of surface tension with time at a *stationary surface*, the Γ–γ relation is used to determine the rate of development of the stationary surface film. (These calculated quantities of adsorbed acid may without disadvantage be a fraction or a multiple of the real amounts.) For a given rate of surface expansion, the amount of adsorbate present on the expanding surface is deduced. The Γ–γ relation is then used to obtain the theoretical tensions at surfaces expanding at known rates, it being therefore assumed in these calculations that no change in the surface activity of an adsorbed molecule occurs during expansion. The calculated tensions are then compared with the experimental values, in which any change in surface activity due to surface expansion will be reflected. The general conclusions concerning the effect of surface expansion on surface activity, reached by this theoretical treatment, agree closely with the effects observed by direct measurement on a solute of similar chain length (Part IX).

FIG. 1.

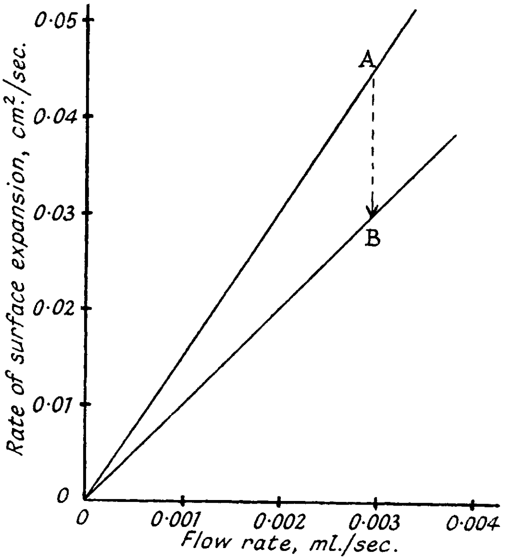
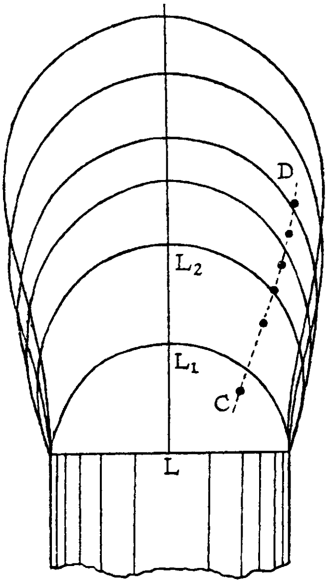


FIG. 2.



EXPERIMENTAL.

Surface Tension–Time Relation for a Stationary Surface.—The technique employed and the results obtained for decoic acid solutions up to the solubility limit of 0·005% (2·91 × 10^{-4}M) have been reported in Part VI (*loc. cit.*). Drops of solution of predetermined volume were formed rapidly on a calibrated orifice. When the tension fell to a value equivalent to the drop weight, the drop fell away, thus recording both surface tension and surface age. By repetition with different initial drop sizes, tension–time curves were obtained (Part VI, Fig. 2) which showed a fall in tension from the value for pure water to the equilibrium tension in time intervals from 10 seconds (2·85 × 10^{-4}M) to 6 minutes (0·466 × 10^{-4}M).

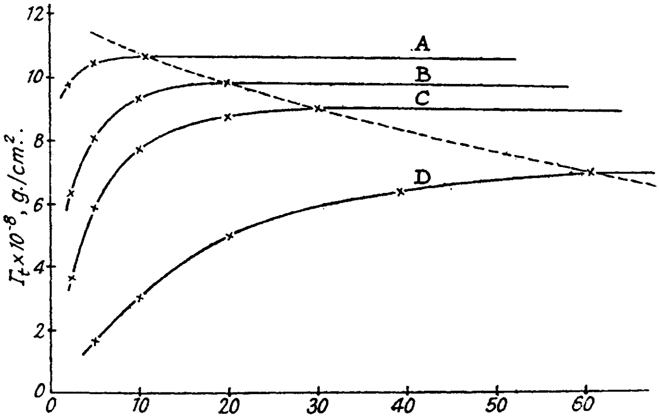
Expanding Surfaces.—It is necessary in these experiments to measure the surface tension without disturbing the surface. The gradual development of a drop of the solution in air satisfies these requirements, and has the advantage that the surface area involved is small, promoting uniformity. The application of this technique to decoic acid solutions has also been described in Part VI (*loc. cit.*). The variation in surface tension of a 1·16 × 10^{-4}M-solution with rate of flow of liquid into the drop is shown in Fig. 9 (experimental curve) and the shape of the curve is similar for all concentrations (Part VI, Fig. 8). The expanding-drop technique has the disadvantage that for a constant liquid-flow rate, the rate of expansion of surface is not uniform throughout the life of a drop. For the orifice used (0·27 cm. outside diameter) the relation between flow rate and rate of surface expansion is shown in Fig. 1. The upper line OA represents the maximum rate of expansion (calculated from the surface-area measurements in Fig. 4) for any given flow rate, and is operative when the drop first forms. As the drop increases under constant flow rate, the rate of surface expansion decreases over range AB to line OB. Nevertheless, the variation in rate of expansion during a drop life does not exceed one-third of the range available by altering the flow rate. It has been found convenient to relate surface tension with rate of flow of liquid, and in calculating the theoretical tensions at the surface of an expanding drop, account is taken of this variation in rate of surface expansion.

Relation between Surface Area and Volume of Expanding Drop.—The image of the drop was projected by means of a long-focal-length achromatic lens on to a distant screen, giving a linear magnification of 21. The orifice was attached to a calibrated capillary tube carrying a mercury thread, and it was thus possible to expel known volumes of liquid. The image was received on a photographic paper screen; the drop volume was increased in stages, and a series of superimposed shapes recorded photographically (Fig. 2). Wires were then fitted to each of the semi-perimeters, and the centroid of each shape obtained by suspending the wire from several points on silk thread. As the drop expands the centroids follow the smooth curve CD, and the positions of these centroids for six different volumes are shown in Fig. 2. The distance of the centroid from the axis of the drop can be measured, and the surface area calculated by Guldinus's theorem.

DISCUSSION AND RESULTS.

Γ-t *Relation.*—The static and dynamic surface tensions of decoic acid solutions at a stationary surface are recorded in Part VI, Fig. 2. The static values have been plotted against the concentration C, and the slope of this curve at various C values substituted into Gibbs's adsorption equation $\Gamma_2^{(1)} = (d\gamma/d \log fC)/\boldsymbol{R}T$ to determine the relation between surface excess Γ of component (2), *i.e.*, decoic acid, and surface tension. The dynamic surface tensions can then be transposed into Γ values, and the curves obtained (Fig. 3) show the development of surface excess with time at 20°. The activity coefficient f has been taken as unity in these calculations. The broken line represents the boundary between dynamic and equilibrium surfaces. Since static tensions were used in deriving Γ_t (Fig. 3), each value of Γ_t represents a surface excess in the state of orientation which holds at a stationary surface.

FIG. 3.



Decoic acid concentration (M).

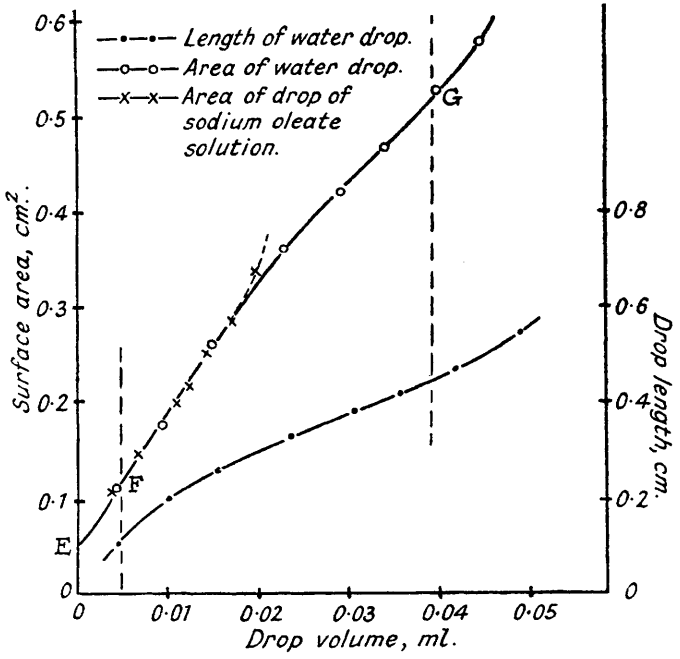
A, 2·85 × 10⁻⁴. B, 1·74 × 10⁻⁴.
C, 1·16 × 10⁻⁴. D, 0·64 × 10⁻⁴.

Surface Area of an Expanding Drop.—The area–volume relation for pure water at 20° is shown in Fig. 4. The curve falls into 3 distinct stages: (1) Represented by EF; in this range the volume is increasing to that of a hemisphere standing on the orifice, and dA/dV is increasing. (2) Represented by FG; this stage approaches closely the form of curve $A = aV^b$ given by an expanding sphere; the constant $a = 5{\cdot}37$ and $b = 0{\cdot}73$ (compared with $a = 4{\cdot}84$ and $b = 0{\cdot}667$ for an expanding sphere). (3) Immediately before falling away, the drop elongates rapidly, and dA/dV again becomes an increasing quantity.

The lower curve (Fig. 4) shows the variation in drop length (*i.e.*, distances LL_1, LL_2, etc., in Fig. 2) with volume, and it is clear that the more rapid increase in area in stage (3) coincides with elongation of the drop. Photographs showed that, with an orifice of 0·27 cm. outside diameter, the liquid remaining outside the plane of the orifice after the falling away of the drop was almost exactly the amount required to form a hemisphere on the orifice, and stage (1) of the curve was therefore not significant in these experiments. For orifice diameters exceeding about 0·4 cm. the remaining liquid is insufficient to form a hemisphere, and stage (1) becomes significant.

During the development of a drop of decoic acid solution, the surface tension changes as well as the drop volume. Since the shape of a pendant drop of given volume varies with the surface tension, it was essential to test the effect of tension changes on the curve in Fig. 4 before the curve could be applied quantitatively. A second curve was therefore obtained by using a sodium oleate solution, $\gamma = 34$ dynes/cm. The experimental points are recorded in Fig. 4. As a result of the low γ value the drop falls away at a lower volume, but the operative second stages of each curve show close agreement. It was also confirmed that within the range of flow rates used, the shape of the drop at any stage was independent of its rate of development.

FIG. 4.



Calculation of Surface Concentration at an Expanding Surface.—During the expanding-drop experiments the solution left the orifice in a series of drops, the drop volume being constant for a given flow rate. The liquid remaining outside the orifice after the release of a drop reverted instantaneously to hemispherical form, so that for each drop the surface area at zero time was that of a hemisphere on the orifice. For a particular flow rate, the area–volume curve (Fig. 4) is readily converted into an area–time curve (not reproduced). Therefore the following information is now available for a given concentration and flow rate : (1) the rate of development of surface excess (Fig. 3) at a stationary surface ; (2) the rate of expansion of the surface, and the rate of development of surface excess at an expanding surface may be deduced as follows :

The expansion of the surface can be regarded for calculation as proceeding in a series of small increments. Thus in the first small interval of time $0 \longrightarrow \delta t$, a surface excess $\delta\Gamma$ will have accumulated at the stationary surface. The surface can then be regarded as expanding instantaneously from A_0 (the area of the hemisphere) to $A_0 + \delta A_0$, and the surface concentration will be reduced to $A_0\delta\Gamma/(A_0 + \delta A_0)$, represented in Fig. 5 by point L. Therefore after period δt the surface condition is equivalent to point S on the stationary curve, and during the second interval $\delta t \longrightarrow 2\delta t$ adsorption will proceed along LM, where LM is parallel to the stationary-surface curve beyond S. The surface now expands $A_1 \longrightarrow A_1 + \delta A_1$ (where $A_1 = A_0 + \delta A_0$) and the surface excess represented by M is thus reduced by the fraction $A_1/(A_1 + \delta A_1)$ to point N. (The fraction by which the surface excess is reduced at the end of each δt period will not be a constant, since the area–time relation is not linear.) The development of Γ at an expanding surface is therefore represented by the broken line through L and N.

The above deductions are based on the assumption that at zero drop life the surface contains no excess of solute. This, however, is by no means certain. The hemisphere of liquid from which the drop starts is formed by contraction of the neck of liquid which joins the orifice and drop immediately before drop release; the initial surface may therefore contain any amount up to that corresponding to the static surface tension. The surface being assumed to have this maximum amount of surface excess at zero time, the variation of Γ with time may be deduced as follows. The full line in Fig. 6 again represents the development of Γ at a stationary surface, and Γ increases to a maximum value (Γ max.) shown at *P*, which now represents the state of the expanding surface at zero time. During the first time interval δt, the surface excess will be reduced to $A_0\Gamma_{\max.}/(A_0 + \delta A_0)$ (point *Q*). Further adsorption will therefore occur, at a rate given by the tangent to the stationary-surface curve at *L*, where *L* represents the average surface concentration during the interval δt. This adsorption will increase the surface excess by an amount $(\mathrm{d}\Gamma/\mathrm{d}t)_L.\delta t$ represented by *QM*. During the second δt interval the surface expansion reduces the surface excess (represented by *M*) by the fraction $A_1/(A_1 + \delta A_1)$ to *N*; adsorption will have proceeded to an amount represented by *NO* and equal to $(\mathrm{d}\Gamma/\mathrm{d}t)_R.\delta t$, where the Γ value

FIG. 5.

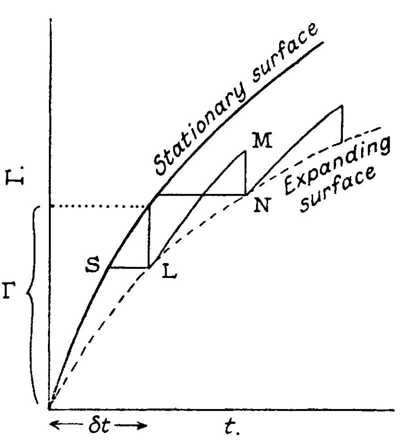


FIG. 6.

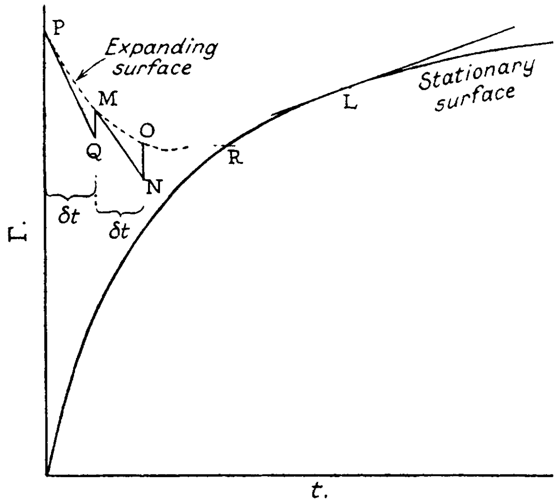
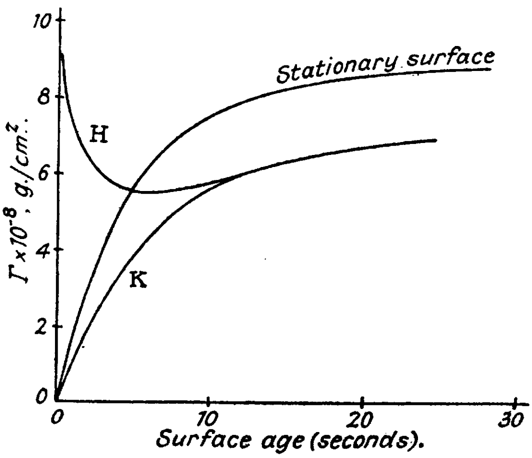


FIG. 7.

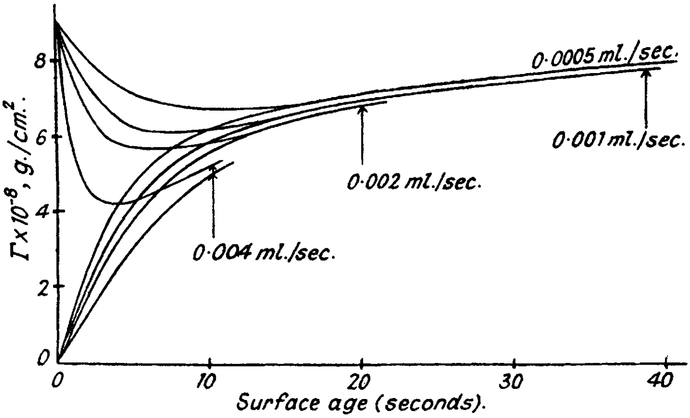


H, *expanding surface with maximum surface excess at zero time.*
K, *expanding surface with no surface excess at zero time.*

of R is the mean of the values for M and N. Therefore if the surface carries its maximum excess of solute at zero time, the variation of Γ will be represented by the broken line PMO.

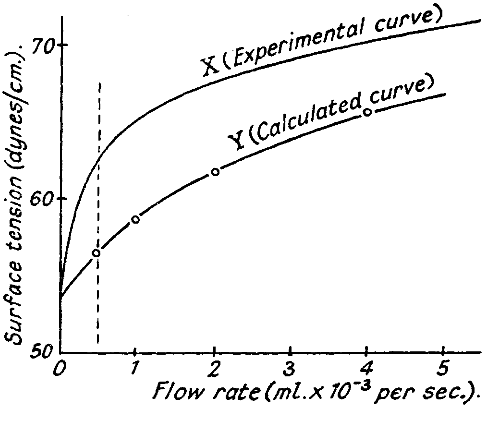
On the above basis, Γ–t curves have been calculated for a 1·16 × 10^{-4}M (0·002%) decoic acid solution, and a flow rate of 0·002 ml./sec. (Fig. 7). Curve K assumes no surface excess, and curve H maximum excess, at zero time, and it is of immediate interest that the two curves coincide at higher t values. It follows that the common part of the curve represents the surface excess whatever the initial condition of the surface may be, and that provided measurements be made over this time range, the initial condition of the surface is of no consequence. In order to verify that this feature was common to all rates of expansion, H and K curves for a concentration of 1·16 × 10^{-4}M have been deduced for the four flow rates 0·0005, 0·001, 0·002, and 0·004 ml./sec., and are collected in Fig. 8. The results indicate that for a given concentration, the surface age at which the curves coincide is little influenced by rate of expansion. However, since the Γ values of the common curves represent a balance between rates of adsorption and surface expansion, slightly higher Γ values are reached at the lower flow rates. The vertical arrows (Fig. 8) are placed on the time axis at the surface age at which the drops would fall away from the 0·27 cm. orifice at each particular flow rate. At flow rates exceeding 0·004 ml./sec., the H and K curves do not coincide before the drop falls away; therefore comparisons between calculated and measured surface tensions have not been made for flow rates in excess of 0·004 ml./sec., since the measured values would not then be independent of the initial condition of the drop surface.

FIG. 8.



Comparison between Calculated and Experimental Surface Tensions.—Fig. 9 (curve X) shows the actual variation in surface tension which occurs in a 1·16 × 10^{-4}M-decoic acid solution when rate of flow of liquid into the drop is varied. It is now possible to deduce this curve theoretically. The following example illustrates the method.

FIG. 9.



At a flow rate of 0·002 ml./sec., the drop weight was 0·0400 g., corresponding to a surface tension of 67·5 dyne/cm., as shown in curve X, Fig. 9. The drop life was 20·0 seconds, and reference to Fig. 8 indicates that after this time the surface contains $\Gamma = 6{\cdot}80 \times 10^{-8}$ g./cm.^{2}. The Γ–γ relation discussed above may then be employed to determine the surface tension corresponding to this excess, when $\gamma = 61{\cdot}7$ dynes/cm. (curve Y, Fig. 9). The remaining points on curve Y are determined similarly.

It is clear that a considerable discrepancy exists, and this is the case with other flow rates and concentrations also. The Γ–γ relation used in determining curve Y was derived using surface tensions measured at a stationary surface, and curve Y thus represents the surface-tension values which would have obtained had the adsorbate present exerted the same surface activity as at a stationary surface. The fact that the experimental tensions are higher indicates that expansion of the surface renders the adsorbed molecules less efficient; *e.g.*, in the above example, the amount of adsorbate present on the expanding surface after 20 seconds lowers the surface tension from the water value (72·8 dynes/cm.) to 67·5 dynes/cm., whereas the same amount of adsorbate would lower the tension to 61·7 dynes/cm. if present at a stationary surface. The following factors may be responsible for this decrease in surface activity: (1) Association of decoic acid molecules may occur as a result of lateral adhesion at the surface. However, such association, which would probably reduce surface activity, is less likely to occur at an expanding than at a stationary surface. (2) The position of the decoic acid molecules with respect to the plane of the surface may differ in the two cases. Thus the hydrocarbon chains, which at a stationary surface may be outside the water surface, may be prevented at an expanding surface from fully penetrating the surface and thus forming a hydrocarbon exterior. (3) The degree of penetration of the surface by the decoic acid chains may be similar in the two cases, but their mean angle of orientation with respect to the surface may differ.

This effect cannot yet be attributed solely to change in angle of orientation, but available evidence supports this view. All soluble films so far studied have been found to be gaseous in state (Adam, *op. cit.*, p. 116). This will almost certainly be the case with expanding films, and it is feasible that orientation should be much more random at an expanding surface. It is significant that very slight surface expansion is necessary to bring about the full decrease in surface activity; at flow rates beyond the broken line in Fig. 9 the two curves are almost parallel. This is in accord with the disorientation hypothesis, since as soon as disorientation has been brought about, the surface activity should be no longer sensitive to further increases in rate of expansion. Again, it has been shown in Part VI (*loc. cit.*) that, while the stationary surface has a high temperature coefficient of tension, the tension at an expanding surface is not sensitive to temperature. The higher order of molecular orientation at a stationary surface is more likely to be subject to kinetic agitation, whereas the molecules adsorbed on an expanding surface, if already disorientated, are unlikely to be influenced appreciably by small changes in temperature.

It is not known to what extent the angle of orientation of adsorbed molecules in a soluble film influences their power to lower the tension (or even whether horizontal or vertical orientation represents the position of highest surface activity), so it is not yet possible to decide whether surface expansion brings the mean direction of the adsorbed molecules nearer the vertical or the horizontal position. From determinations of the work of adsorption in homologous series, Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1883 *et seq.*) deduced that adsorbed straight molecules in a stationary, soluble film lie parallel with the surface, and calculated (3rd Colloid Symposium Monograph, 1925, 75) that this position represents the lowest energy state. The general applicability of Langmuir's conclusions being assumed, then horizontal orientation represents the position of maximum surface activity, and the adsorbed molecules are deflected from this position during surface expansion. Evidence has been produced in Part IV (*J.*, 1945, 98) that long-chain molecules during migration to the surface are orientated with their hydrocarbon chains directed towards the surface. The adsorbate molecules may therefore penetrate a stationary surface in this direction, and then fall to the horizontal position of least energy. However, such a molecule penetrating an expanding surface may be prevented, by the impact of water molecules also arriving at the surface, from assuming the horizontal position.

The experiments on sodium dodecyl sulphate solutions described in Part IX (following paper) indicate that the decrease in surface activity on expansion of the surface is of the same order as for decoic acid. This supports the belief that the decrease is a function of chain length rather than of polar group or degree of ionisation.

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