180. *The Properties of Freshly-formed Surfaces. Part IX. Expansion of Soluble Films of Sodium Dodecyl Sulphate at Air–Water and Toluene–Water Interfaces.*

By C. C. Addison and S. K. Hutchinson.

The deduction in Part VIII (preceding paper), that the surface activity of adsorbed long-chain molecules is decreased on expansion of the surface, is supported experimentally by measurements of the surface tension of aqueous solutions of sodium dodecyl sulphate at both stationary surfaces (by the vertical-plate method) and expanding surfaces (by the drop-weight method). Differences (up to 10 dynes/cm.) occur at all concentrations below 0·02M, and are attributed to disorientation of the adsorbed molecules during surface expansion. Interfacial-tension measurements against toluene show similar differences for solutions below 0·005M, but at higher concentrations surface expansion has no influence on the behaviour of the surface film. This is consistent with the anchoring effect of the toluene phase on the carbon chains, and a suitable explanation is again possible on the basis of disorientation.

It has been deduced in Part VIII (preceding paper) that expansion of a soluble film of decoic acid results in a decrease in the surface activity of the adsorbed molecules. The work now described was carried out in order to determine whether this decrease was common to other long-chain compounds, and to obtain direct experimental evidence of the surface-expansion effect. Some evidence of its existence is already available; for instance, the surface tensions of solutions of short-chain compounds (up to about C_5) determined by the vertical-plate and the drop-weight method show exact agreement (and the drop weight of such solutions is independent of the rate of formation of the drop), whereas the surface-tension values for a range of soap solutions (Cavier, *Compt. rend.*, 1941, **212**, 1146) and for solutions of bile (Boutaric, Berthier, and Roy, *Bull. Soc. Chim. biol.*, 1940, **22**, 170) measured by the ring-detachment method are as much as 8 dynes/cm. lower than the values obtained by the drop-weight method. Comparisons made during this work between the tension values given by the vertical-plate and the ring-detachment method for some long-chain compounds have indicated fairly close agreement. Therefore in some cases the expansion of a surface during detachment of a ring makes only slight difference to the recorded tension, presumably because the ring is already becoming detached before appreciable surface expansion occurs, and the discrepancies noted by Cavier (*loc. cit.*) may be due to surface expansion.

The changes in surface tension of decoic acid solutions on expansion of the surface have been attributed to two factors, *viz.*, the slow development of diffusion equilibrium and the change in orientation at an expanding surface. In order to make a separate experimental study of the second factor it is clearly essential to employ solutions in which any fall in surface concentration resulting from surface expansion is immediately replenished by diffusion from bulk solution. Sodium dodecyl sulphate was selected for these experiments because (*a*) having 12 carbon atoms, its migrational velocity will be high, and its high solubility permits its use in such concentration that the time required for the establishment of diffusion equilibrium is negligible, (*b*) hydrolysis does not occur, (*c*) the alkyl sulphates are completely dissociated in solution (Howell and Robinson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 386), and (*d*) there is little doubt that the single long-chain ions represent the surface-active species (Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243). Therefore any discrepancy between tension measurements at stationary and expanding surfaces must arise directly from expansion of the film. Considerable discrepancies have been found to occur at both air–water and toluene–water interfaces, and can be satisfactorily explained on the basis of molecular disorientation.

<div align="center">EXPERIMENTAL.</div>

The surface and interfacial tensions at stationary surfaces were measured by the vertical-plate method described in Part VII (this vol., p. 930). Results were not reproducible if the platinum plate was wiped with filter-paper between each determination, because of the extreme sensitivity of these solutions to traces of metal ions. No such difficulties were encountered when a fine cloth, previously boiled in distilled water, was used. Surface tensions at expanding surfaces were measured by allowing drops of the solution to form gradually in air, and the rate of flow of liquid into the drop was controlled as described in Part VI (*J.*, 1946, 579). A similar technique was employed for interfacial tensions; the orifice was immersed in toluene, and the drop volume determined by counting the number of drops required to empty a calibrated bulb in the pipette. The same orifice was used as for the decoic acid experiments (Part VIII) and had an outside diameter of 0·27 cm. The major changes in tension were found to occur when the surface was expanding very slowly, and this involved a drop life of 10—15 minutes. To avoid loss by evaporation during the surface-tension measurements, the orifice tube was inserted through the stopper of a small weighing bottle containing water, thereby enclosing an air space of about 8 ml.; 15 minutes were allowed

for this volume to become saturated with water vapour, and the drops were then formed at a distance of approximately 0·5 cm. from the water surface. With these precautions, drop weights were exactly reproducible.

The sample of sodium dodecyl sulphate used was recrystallised several times from absolute alcohol, washed with light petroleum (b. p. 80—100°), and dried in a vacuum. Solutions were prepared in carbon dioxide-free water twice redistilled in Pyrex glass from phosphoric acid solution. The critical concentration for micelle formation in these solutions is highly sensitive to impurities; the value obtained by the vertical-plate method (0·0065M) is in close agreement with the accepted value (Powney and Addison, *loc. cit.*) and serves as a guarantee of purity.

All experiments were carried out at 15° ± 0·5°.

DISCUSSION AND RESULTS.

The variation in the surface tensions of sodium dodecyl sulphate solution with rate of expansion of the drop is shown in Fig. 1 for concentrations in the range 0·001—0·02M. The

FIG. 1.
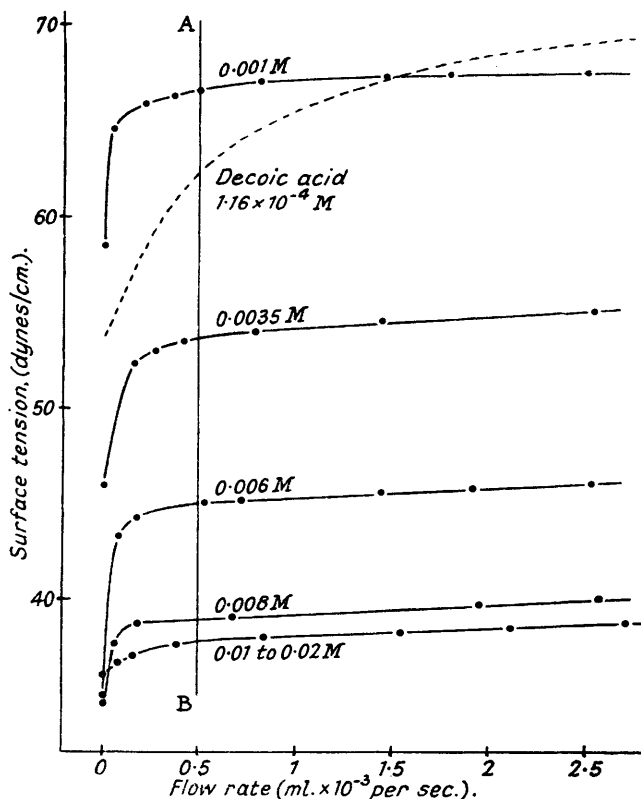
tensions at zero flow rate are those for the stationary surface as measured by the vertical plate, and the remaining tensions are determined by the expanding-drop method. The curves fall into two distinct sections divided by line *AB*, *viz.*, a rapid rise in tension immediately the surface begins to expand, followed by a slight increase (of the order of 1 dyne/cm. over the full flow-rate range), which is independent of concentration. The general shape of curve is the same for all concentrations studied, and there is no change in behaviour at the critical concentration. The following possible explanations must be considered.

(1) The surface tension of solutions of sodium dodecyl sulphate decreases with ageing of the surface. Since slow drop formation involves long drop life, the possibility arises that the lower tensions at slow flow rate may be due to this effect. However, the ageing of the surface is attributed (Alexander, *Trans. Faraday Soc.*, 1941, **37**, 15) to rearrangements in the established surface film. This is unlikely to occur at an expanding surface, and furthermore the tension values are all higher than, and fall to, the vertical-plate value determined at a fresh surface.

(2) The fall in concentration in the surface film may not be immediately replenished by

diffusion from bulk solution. However, if the time taken for replenishment of the surface is appreciable, the concentration in the surface layer depends upon the rate of surface expansion, and tension is a function of flow rate throughout the whole available flow-rate range. These conditions are known to hold for decoic acid, and a typical curve is superimposed in Fig. 1 for comparison. The dodecyl sulphate curves cannot be explained on the basis. Throughout the greater part of the flow-rate range the tension shows little change, and the γ–flow rate relation is linear. The rapid increase in γ with initial expansion of the surface would imply that the establishment of diffusion equilibrium in these solutions was slower than for decoic acid solutions whereas the vertical-plate measurements show no appreciable drift. Again, it is significant that the increase in tension on expansion is of the same order as that deduced for decoic acid solutions, where changes in tension due to diffusion have been taken into account.

FIG. 2.
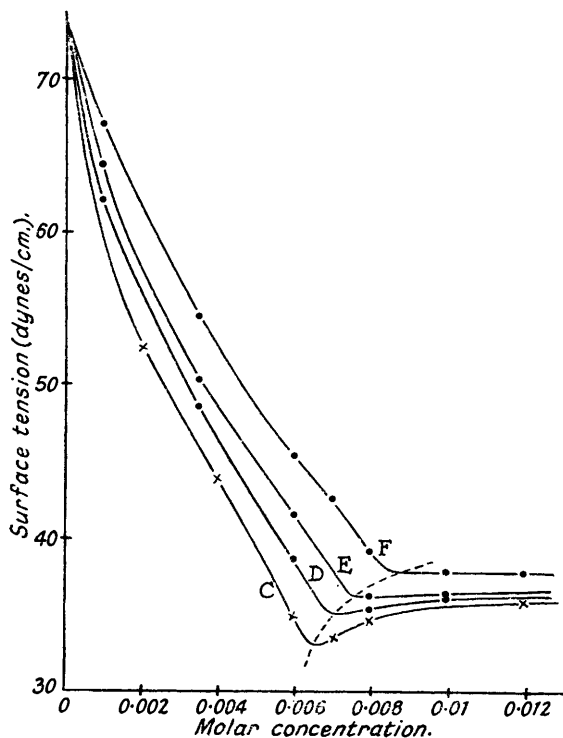
Curve.	Method.	Flow rate, ml. $\times 10^{-3}$/sec.
C	*Vertical plate.*	—
D	*Drop weight.*	0·02
E	,,	0·04
F	,,	1·0

(3) Since the surface film is composed of the single long-chain ions, surface expansion may alter the distribution of electric charge at the surface. The possibility cannot yet be entirely discounted, but the fact that the increases in tension are of the same order as those deduced for decoic acid, where the surface film is composed of un-ionised acid molecules, suggests that this factor is not significant.

These curves may, however, be suitably interpreted on the basis of change in orientation. Thus the adsorbed molecules, orientated horizontally at a stationary surface in their position of highest surface activity, may be considered as being disorientated by surface expansion, so that the mean position of the carbon chains is at an angle to the surface, and in a position of lower surface activity. (Such a change in orientation should be reflected in a change in surface potential, and this aspect is being investigated.) It has been calculated in Part VIII (*loc. cit.*) that the slight expansion of a decoic acid film equivalent to a flow rate of 0·5 × 10⁻³ ml./sec. was sufficient to produce the full loss of surface activity, and Fig. 1 indicates that the initial rapid

change in tension of sodium dodecyl sulphate solutions is complete within the same narrow range of flow rate. Thus evidence is now available that soluble films of long-chain compounds terminating in the polar groups CO_2H, CO_2Na, or SO_4Na each show a change in tension of up to 10 dynes/cm. on expansion. It appears probable that the chain, rather than the polar group, is therefore responsible, and an investigation into the influence of chain length is in progress.

Tension–Concentration Curves at Stationary and at Expanding Surfaces.—The full curve relating concentration of sodium dodecyl sulphate with the surface tension at 15°, measured by the vertical plate, is shown in Fig. 2 (curve *C*). The curve is similar in position to that determined by Powney and Addison (*loc. cit.*) by the ring method, and shows a break at the same critical concentration (0·0065M). The corresponding curves for surfaces expanding at three different rates also show breaks which move to higher concentrations as the flow rate increases. Surface expansion can involve no change in the distribution of solute in bulk solution between the single ion and the micellar state, and therefore the apparent increase in critical concentration must be

FIG. 3.
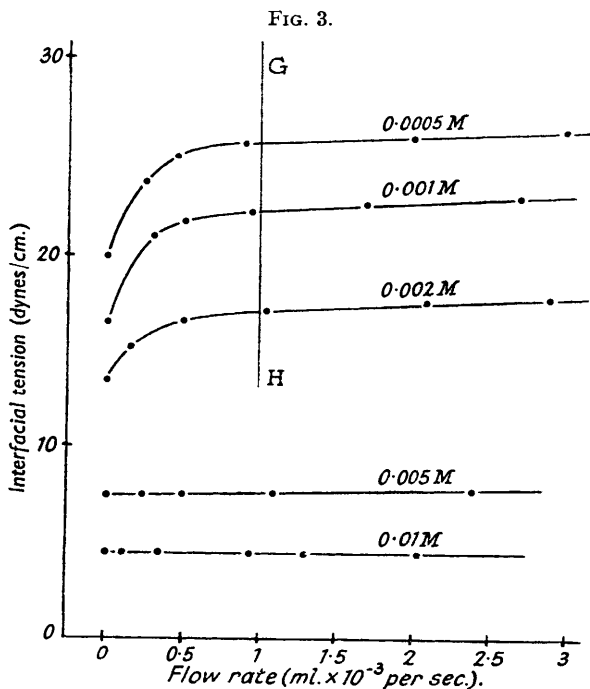
a purely surface effect. The micelles contribute little to the surface activity at a stationary surface, but they may become active at an expanding surface. Again, micellar aggregation is weak, and conversion from the micellar into the single-ion state is readily achieved (*e.g.*, by dilution of the solution) so that some of the micelles which arrive at an expanding surface may be dissociated into single ions.

Expanding Films at Interfaces.—At the interface between water and organic liquids, the adsorbed carbon chains enter the organic liquid, and their mean position is therefore at an appreciable angle to the plane of the interface. The lowering of tension is determined by the extent to which the adsorbed molecules can form a bridge between the two phases, and this depends upon both the polar nature of the end group and the chain length. The organic liquid has an anchoring effect on the carbon chains and therefore, if the decrease in surface activity on expansion of an air–liquid interface is to be attributed to disorientation of the adsorbed molecules, the expansion of a liquid–liquid interface might be expected to influence the interfacial activity to a lesser degree.

Interfacial tensions at stationary and at expanding surfaces have been measured against toluene at 15° for a range of sodium dodecyl sulphate solutions, by the vertical-plate and the drop-volume method respectively, and the results are shown in Fig. 3. For the dilute solutions below 0·005M the curves have a shape similar to the corresponding surface-tension curves. The points at zero flow rate represent vertical-plate measurements, and a rapid rise in interfacial

tension takes place almost immediatley upon expansion of the surface, followed by a slight and uniform rise (about 1 dyne/cm.) throughout the remaining available flow-rate range.   The effect disappears at concentrations beyond 0·005M, both methods of measurements then being in close agreement.   At 0·005M, surface expansion changes the tension by only 0·4 dyne/cm., and at 0·01M exactly reproducible results were obtained irrespective of method or rate of surface expansion.   The full interfacial tension–concentration curves are shown in Fig. 4; they show a break at the same critical concentration as for the stationary surface-tension curve in Fig. 2, but the stationary and the expanding-surface curves now coincide beyond 0·005M.

It is again possible to explain these curves on the basis of disorientation.   In dilute solution the adsorbed molecules may be considered as isolated units, virtually uninfluenced by lateral cohesive forces.   Owing to the attraction of the organic phase for the carbon chains, their orientation at the stationary surface will be nearer vertical than horizontal.   During expansion of the interface these molecules must travel laterally, and such a molecule could only maintain its

FIG. 4.

Curve.	Method.	Flow rate, ml. $\times$ 10^{-3}/sec.
K	*Vertical plate.*	—
L	*Drop volume.*	1·0
M	,,	0·2
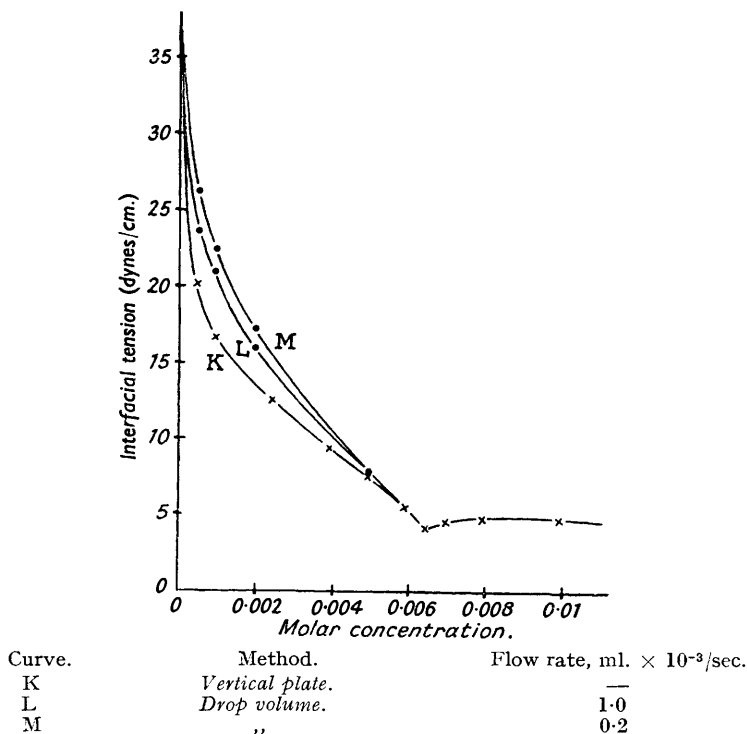
vertical orientation if it was so distributed across the interface that viscous and frictional resistance were equal in the two phases.   The state is unlikely, since the longer carbon chains will be predominantly in the organic-liquid phase, so that the lateral motion must result in a different (and probably random) orientation at a mean angle nearer to the horizontal, with consequent decrease in the interfacial activity.   The rate of surface expansion (equivalent to a flow rate of 1 × 10⁻³ ml./sec.) required to produce the full initial increase in tension at the liquid–liquid interface (line *GH*, Fig. 3) is twice the rate required at the air–liquid interface, and this is consistent with the anchoring effect of the toluene phase on the carbon chains.   The change in orientation during lateral motion is likely to diminish as the concentration in the aqueous phase, and thus the number of adsorbed molecules, increases.   It is significant that the expanding- and the stationary-surface curves (Fig. 4) only coincide at the lowest tensions; if the surface film then approaches a close-packed monolayer the lateral cohesion will resist any pronounced change in angle of orientation.

Trough Experiments.—Although the vertical-plate results (Figs. 1 and 3) clearly form the limiting points on the expanding-drop curves for zero flow rate, it seemed desirable to confirm that increase in surface tension with expansion of surface could be observed over the full tension

range when the same technique of measurement was used throughout. Solutions of sodium dodecyl sulphate were therefore placed in a trough, and the surface confined to a known area by a movable barrier. The vertical plate was then inserted into the surface, and wetted above the meniscus line to enable the plate to record increases in surface tension by entering the liquid without change of contact angle (Part VII, *loc. cit.*). On increase of the surface by means of the movable barrier, the vertical plate recorded an increase in surface tension, and preliminary experiments indicate that this increase is of the same order as those recorded in Figs. 1 and 3. When the movement of the barrier ceased, the tension decreased within a few seconds to the original value; details of these experiments will be described later.