711. *The Properties of Freshly Formed Surfaces. Part XIV. Further Studies of the Influence of Surface Expansion on Soluble Films of Long-chain Compounds.*

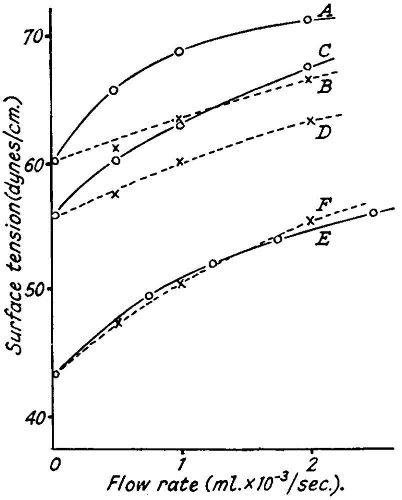
By C. C. Addison and S. K. Hutchinson.

Investigations on the effect of surface expansion on the properties of soluble films reported in earlier parts of this series have been extended by measurements of the surface tension, at expanding surfaces, of solutions of decyl alcohol and decoic acid over the full concentration range. Both expanding-drop and moving-barrier methods have been used. The latter method, in conjunction with the vertical plate, gives a continuous record of the tension during surface expansion. Both methods indicate that at high solute concentration there is close agreement between measured and predicted values, thus confirming the methods of calculation given in Part VIII (*J.*, 1948, 936). Discrepancies which occur in dilute solution only are attributed to the greater ease with which disorientation can occur in the surface film as the area per molecule increases. The low values observed for the temperature coefficient of surface tension at expanding surfaces of dilute decyl alcohol solutions support this view.

It was reported in Part IX (*J.*, 1948, 943) that expansion of the soluble film at the surface of aqueous solutions of sodium dodecyl sulphate resulted in an increase of as much as 10 dynes/cm. in the measured surface tension. There is no reason to suppose that in these experiments the surface expansion caused a decrease in surface excess, and the increase in tension has been attributed to disorientation of the adsorbed molecules during surface expansion. This effect almost vanishes when the concentration is increased above that required for micelle formation (0·006 M.) but it is not possible to deduce from the results in Part IX whether this is due to formation of micelles or merely to an increase in concentration. In Part VIII (*J.*, 1948, 936) it was observed that a discrepancy of up to 6 dynes/cm. occurred between surface tensions of aqueous decoic acid solutions measured by the expanding-drop method, and the tensions calculated from stationary surface adsorption curves and measured expansion rates. Results for only one dilute solution were given, although the effect was known to occur with all dilute solutions. In view of the above it was clearly necessary to investigate the influence of surface expansion throughout the full concentration range, in systems in which micelle formation does not occur.

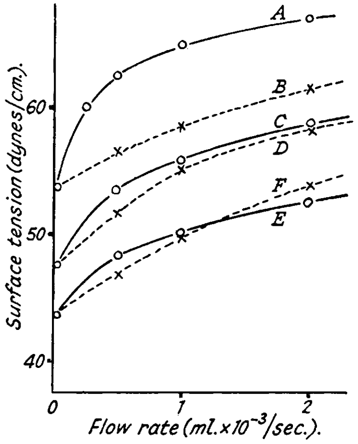
Both decyl alcohol and decoic acid provide suitable systems, and expanding-drop measurements at 20° on solutions of these two substances are given in Figs. 1 and 2. The full curves trace the variation of surface tension with rate of flow of solution into the drop, and the broken curves show the corresponding variations calculated by the method given in detail in Part VIII (*loc. cit.*). Stated very briefly, the method of calculation is as follows: If the surface area A increases by a known amount δA in time δt, the surface excess Γ will decrease by an amount $\delta\Gamma_1$, which can be calculated. This is partly compensated by the adsorption $\delta\Gamma_2$ which occurs during δt, so that $\delta\Gamma_1 - \delta\Gamma_2$ represents the change in Γ during unit interval of time. If the rate of adsorption to the stationary surface is known, this scheme may be developed stepwise to give the change in tension (or Γ) throughout the expansion process.

FIG. 1.



Curves.	*Decyl alcohol concn.*, %.
A, *B*	0·00062
C, *D*	0·00092
E, *F*	0·0020

FIG. 2.

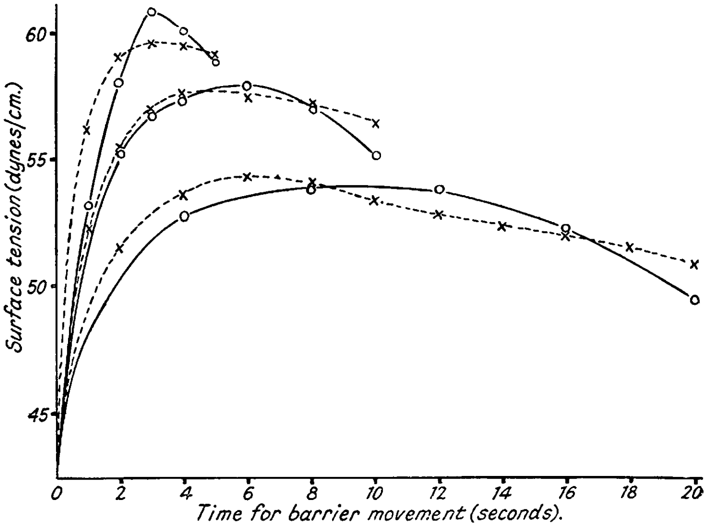


Curves.	*Decoic acid, concn.*, %.
A, *B*	0·0020
C, *D*	0·0030
E, *F*	0·0042

The results given in Figs. 1 and 2 are closely similar, and in each case the experimental and the calculated tensions at the higher concentration are in satisfactory agreement. As the concentration diminishes, the discrepancy between experimental and calculated tensions increases, but must ultimately fall again towards zero in extremely dilute solutions. In each case there is therefore a large part of the concentration range (approx. 0·0015 to 0·0036% for decyl alcohol and 0·003 to 0·005% for decoic acid) over which agreement is satisfactory. This agreement is a matter of some importance since, if fully established, it provides valuable support for the validity of the assumptions made in deriving the calculated tensions. These assumptions are discussed later in this paper.

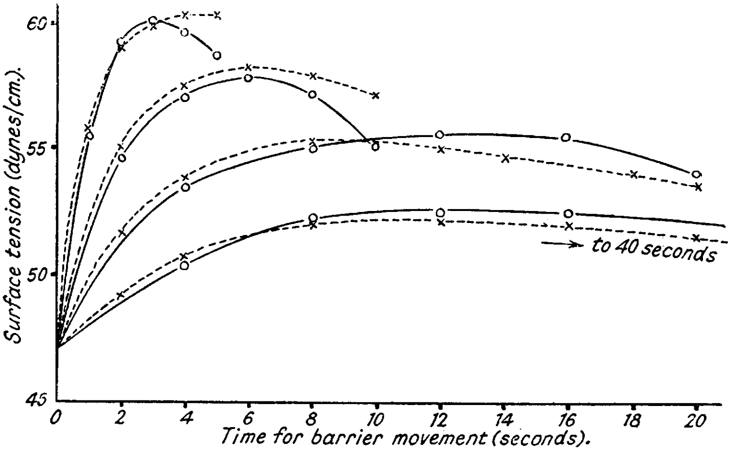
Trough Experiments.—At this stage it seemed desirable to obtain independent confirmation of the results given in Figs. 1 and 2. During expansion of a drop, the tension is continually changing, but by the drop-weight technique it is not possible to obtain for a particular flow rate more than a single point on the tension–expansion rate curve. However, by using a rectangular trough and vertical plate it is possible to record the surface tension throughout the full expansion period. The trough used was that already described in Part XIII (preceding paper) and gave a liquid surface area 10 × 6·43 cm. In each experiment the trough was filled with the appropriate solution, and the barrier was then placed in such a position (parallel to the shorter edge of the trough) that it enclosed a liquid surface area of 15·8 cm.^{2}. The vertical plate was then inserted into this area, and the surface allowed to reach equilibrium tension. Since expansion of the surface involves an increase in tension the vertical plate enters more deeply into the solution. In order to maintain zero contact angle, the plate was wetted to a distance slightly greater than that equivalent to the expected tension rise by dipping it momentarily into the solution immediately before movement of the barrier. The barrier was then moved, at a constant rate, through a distance of 5·9 cm. to expand the surface area to the upper limit of 53·7 cm.^{2}. All the experiments described below were identical except that different time intervals were employed for the movement of the barrier between its standard limits. The time intervals were chosen so as to give rates of surface expansion of the same order as those which occur with the expanding drops. Since the barrier was moved with constant velocity, the rate of change of area (per unit area of surface) gradually diminished during expansion of the surface. The ranges employed are compared in the following table with the corresponding ranges which are involved in the expanding drop method (Figs. 1 and 2).

Fig. 3.



0·002% *Decyl alcohol solution.*

Fig. 4.

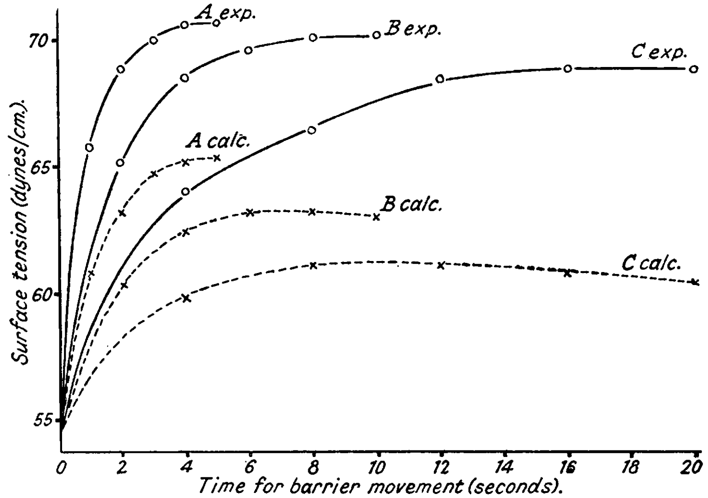


0·003% *Decoic acid solution.*

Trough method.		Expanding-drop method.	
Time for barrier movement (secs.).	Range of expansion rates (% change in area per sec.).	Liquid flow rate (ml. × 10^{-3}/sec.).	Range of expansion rates (% change in area per sec.).
5	47·8 → 14·1	3	31·4 → 5·7
10	23·9 → 7·1	2	23·6 → 4·3
20	12·0 → 3·5	1	12·7 → 2·3
40	6·0 → 1·8	0·5	5·6 → 1·0

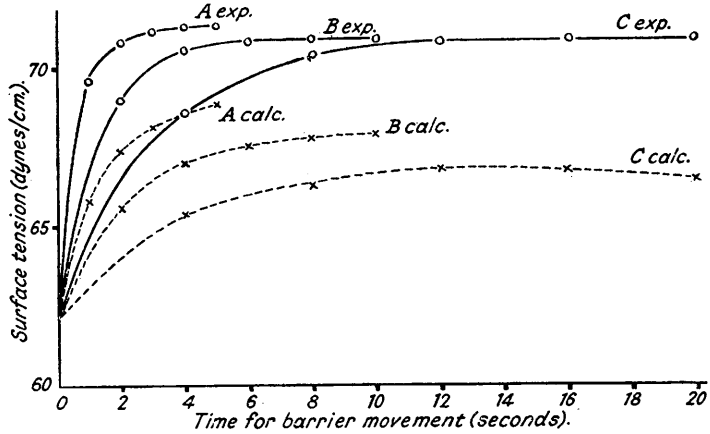
The variation of surface tension which occurs with movement of the barrier is plotted as full lines in Figs. 3 and 4 for various barrier velocities. The measurements were carried out at 20°, and the concentrations of decyl alcohol and decoic acid respectively are those at which agreement between calculated and experimental tensions was obtained by the expanding-drop method. The broken curves represent the tension changes predicted by the method given in Part VIII (*loc. cit.*), the appropriate adsorption curves and the expansion rates shown in the above Table being employed. In view of the rapidity with which it is necessary to record the measured surface tensions (and consequently the greater experimental error involved) the agreement between the calculated and the experimental values in Figs. 3 and 4 is regarded as quite satisfactory.

FIG. 5.



0·001% *Decyl alcohol solution.*

FIG. 6.

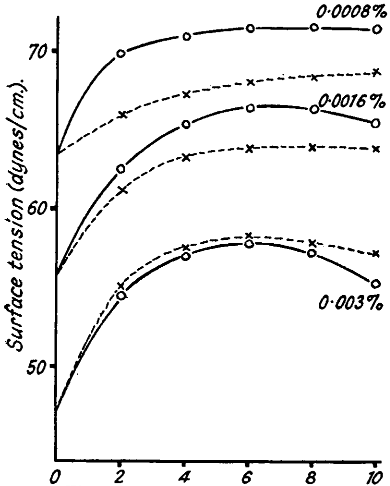


0·0005% *Decyl alcohol solution.*

The trough method has also been used to confirm the discrepancy which occurs in more dilute solutions. Figs. 5 and 6 show experimental and calculated tension values at 20° for two dilute solutions of decyl alcohol at various expansion rates, and in each case the discrepancies are seen to be considerable. It would appear from Figs. 5 and 6 that the discrepancy increases when the barrier velocity is diminished, but this is probably a false picture. When the barrier velocity is decreased, there is more time for adsorption to occur and as a result the calculated tensions are lower. On the other hand, the measured tensions increase almost to the water value (and reach this high value more quickly for greater barrier velocities) but cannot rise above this value, so that the discrepancies are unlikely to be a true measure of the loss of surface activity on expansion of the surface. Similar results obtained for dilute decoic acid solutions at 20°, with a 10-second expansion interval throughout (Fig. 7), give further confirmation that the discrepancies arise only in more dilute solutions.

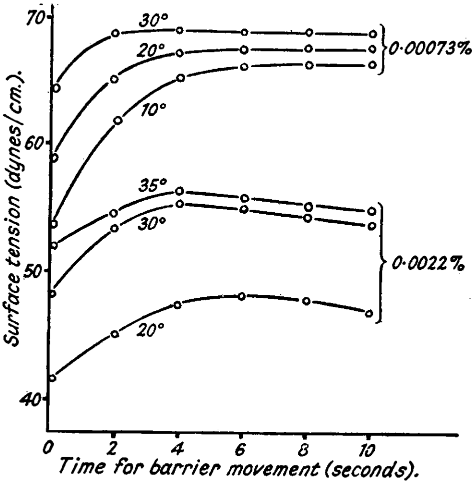
The effect appears to be predominantly a function of chain length, since the substitution of the CO_2H by the $CH_2{\cdot}OH$ group introduces no appreciable modification into the system. The experimental work has been extended to similar studies on shorter-chain alcohols; it was found that dilute solutions of *n*-octyl alcohol show a slight surface expansion effect, up to about 2 dynes/cm. at the higher expansion rates, but there was no detectable effect with the lower straight-chain alcohols. It is noteworthy that the surface tensions of solutions of *sec.*-octyl alcohol measured at the rapidly expanding surface of a jet (Part X, in the press) are in agreement with values calculated from stationary surface adsorption curves and measured expansion rates.

FIG. 7.



Decoic acid solutions.

FIG. 8.



Decyl alcohol solutions.

Interpretation of the Expansion Effect.—The trough measurements described above may be regarded as establishing beyond reasonable doubt that for the more concentrated solutions employed the assumptions made in deriving the calculated tension values were justified. Two major assumptions are involved : (*a*) the surface activity of adsorbed molecules is not influenced by expansion of the surface, and (*b*) for a particular bulk concentration and surface excess the rate of adsorption is also independent of surface expansion. In the more dilute solutions at which the discrepancies occur, one or both of these assumptions must be presumed to be invalid. Since assumption (*b*) appears to be justified over a large part of the concentration range, it seems unlikely that there should be any fundamental change in the mechanism of adsorption on dilution of the solution. The discrepancies are more readily interpreted by considering the decrease in surface activity to be due to disorientation of the adsorbed molecules by surface expansion (as already suggested in Parts VIII and IX, *locc. cit.*). In more concentrated solutions the surface film approaches a monolayer; *e.g.*, Γ equilibrium for a 0·002% solution of decyl alcohol is $11{\cdot}6 \times 10^{-8}$ g./cm.^{2} compared with the monolayer value of $12{\cdot}2 \times 10^{-8}$ g./cm.^{2}, and under these conditions there will be little opportunity for disorientation. However, as surface area per molecule increases with falling concentration, it is possible for disorientation to occur to an increasing degree. Similar considerations apply to the shorter-chain compounds, but the shorter chains can probably recover their equilibrium orientation more readily.

The high temperature coefficients of surface tension which are obtained for stationary surfaces of decyl alcohol solutions have been discussed in Part XII (this vol., p. 3395). It seems probable that the high coefficient may be due, at least in part, to the ready disorientation of adsorbed molecules caused by increase in temperature. It has been shown in Part VI (*J.*, 1946, 579) for dilute decoic acid solutions that this high coefficient almost disappears on expansion of the surface. Since this change in coefficient provides useful support for the disorientation hypothesis, temperature coefficients at expanding surfaces for two concentrations of decyl alcohol have been determined by the trough method, and the results are shown in Fig. 8. For the 0·0022% solution, for which it is considered that disorientation does not occur, the stationary surface temperature coefficient is maintained throughout the surface expansion, and it is only at the higher temperature (30—35°), where the tension is approaching the range for disorientation, that the temperature coefficient shows any appreciable decrease. For the 0·00073% solution, where surface expansion is considered to give rise to disorientation, the temperature coefficient is reduced by a factor of more than 4.

THE UNIVERSITY, NOTTINGHAM.

[*Received, July 22nd*, 1949.]