603. *The Properties of Freshly Formed Surfaces. Part XVI. Dynamic Tensions of Sodium Dodecyl Sulphate Solutions at the Surface of Liquid→Air and Liquid→Liquid Contracting Jets.*

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The variations in tension at the surface of contracting jets of (*a*) sodium dodecyl sulphate solution flowing into air, and (*b*) carbon tetrachloride flowing into aqueous solutions of sodium dodecyl sulphate, have been determined by the methods given in Parts X (*J.*, 1949, 2789) and XV (preceding paper). The tension changes are related to the rapid changes in surface area which occur at the jet surface, and alter in character as well as degree with increasing concentration of solute. The measurements are unique in that the rates of surface expansion are equal to, or may exceed, the rates of adsorption from bulk solution, so that the recorded tensions represent the balance between these two factors.

The expansion or contraction of a soluble film of sodium dodecyl sulphate influences the measured surface tension, and some aspects of this effect have already been considered. In Part IX (*J.*, 1948, 943) it was shown that tensions measured at the surface of an expanding drop could be as much as 10 dynes/cm. greater than the value measured at a stationary surface by the vertical-plate technique. Since the rates of expansion available by the drop method are small, it was not possible to regard the higher tensions as arising from any decrease in quantity of solute at the surface, and the differences in tension were attributed to the disorientation of molecules adsorbed at the expanding surface. The rates of surface expansion available by the trough–moving-barrier method are also small (Part XIV, *J.*, 1949, 3406); when an equilibrium film of sodium dodecyl sulphate solution in a trough is expanded by movement of the barrier an increase in tension does occur, but, in view of the rapid adsorption rates of this compound, the tension change is again regarded as a property of the film.

In dynamic systems it is of interest to study the balance between rates of adsorption from bulk and rates of surface expansion. It was possible to do this with decyl alcohol solutions (Part XIV, *loc. cit.*) by the moving-barrier method, since the rate at which the surface could be denuded of solute by expansion was of the same order as the rate at which the deficit could be replenished by adsorption. However, the rates of adsorption in sodium dodecyl sulphate solutions are so greatly in excess of those for decyl alcohol that in order to carry out similar studies it is necessary to employ a method giving considerably greater expansion rates. Table I compares the expansion rates available by three methods.

Table I.

Method.	Experimental conditions.	Expansion rate; 1 cm.^{2} expands in 1 sec. to :
Expanding drop	Liquid flow rate 3×10^{-3} ml./sec.; orifice radius 0·135 cm.	1·3 cm.^{2}
Trough and moving barrier	Maximum practicable rate of barrier movement	1·5 cm.^{2}
Contracting jet	Orifice radius 0·747 cm.	20 cm.^{2}

The experimental results given below indicate that the rates of expansion available in the contracting jet are sufficiently large to equal, or even to exceed, the rates of adsorption of sodium dodecyl sulphate molecules from solution, and in this paper these effects are compared at liquid–air and liquid–liquid interfaces.

Jets of Sodium Dodecyl Sulphate Solution into Air.—The experimental technique employed was that described in Part X (*J.*, 1949, 2789). The dimensions of the jets given by solutions of four different concentrations are recorded in Table II, where h represents distance from the orifice and r the horizontal radius.

The surface ages at the various points on the jets are included in Table II in order that the tension–h curves given in Figs. 1 and 2 may be transcribed on a time basis. By use of the data in Table II, surface tensions have been calculated by the method given in Part X [*loc. cit.*, equation (8)]. This method involves (*a*) measurement of jet dimensions at the point at which the surface tension is required, and (*b*) evaluation of the total energy of unit mass of liquid at some convenient point in the jet. Since the surface energy at any point on a curved surface is represented by $\gamma\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$, where r_1 and r_2 are the external and internal radii respectively, exact values for these radii are required. The order of accuracy represented by the dimensions in Table II has been found adequate to ensure accurate surface tension values. Concerning (*b*) above, the total energy term is the sum of the kinetic, potential, pressure, and surface energies, and it is of interest that variations in the total energy term ($-K_f$ in equation 8, Part X) influence the calculated tensions to a smaller degree. Table III shows the tensions calculated (for one particular jet) from the h and r values given, with total energy values over the range 145 to 165 ergs. Since K_f can be determined with an accuracy of at least ± 2 units, it is clear that any such deviations in K_f have no significant influence on the calculated tensions; and calculations similar to those in Table III which have been carried out on other jets show that this is true irrespective of concentration or flow rate. In consequence, the surface and the interfacial tension values recorded in this paper are regarded as reflecting accurately the surface properties of the films.

TABLE II.

Jet dimensions : sodium dodecyl sulphate solution → air.

(1) f = 1·256 ml./sec.; c = 0·00109M.

h (cm.).	r (cm.).	Surface age (sec.).
0	0·7471	0
0·050	0·5360	0·053
0·150	0·3880	0·103
0·200	0·3400	0·122
0·250	0·3056	0·133
0·284	0·2875	0·141
0·334	0·2616	0·149
0·434	0·2197	0·163
0·534	0·1922	0·175
0·634	0·1710	0·183
0·834	0·1425	0·195
1·034	0·1250	0·204
1·234	0·1167	0·211

(2) f = 1·335 ml./sec.; c = 0·00217M.

h (cm.).	r (cm.).	Surface age (sec.).
0	0·7471	0
0·050	0·5200	0·045
0·100	0·4350	0·071
0·150	0·3770	0·090
0·222	0·3125	0·110
0·312	0·2628	0·128
0·412	0·2198	0·142
0·512	0·1902	0·152
0·612	0·1705	0·159
0·712	0·1539	0·165
0·812	0·1436	0·171
0·912	0·1354	0·176
1·062	0·1258	0·181
1·212	0·1178	0·187

(3) f = 1·555 ml./sec.; c = 0·00326M.

h (cm.).	r (cm.).	Surface age (sec.).
0	0·7471	0
0·050	0·5180	0·039
0·150	0·3770	0·077
0·254	0·2945	0·101
0·354	0·2400	0·115
0·454	0·2067	0·125
0·554	0·1839	0·135
0·654	0·1660	0·139
0·754	0·1522	0·145
0·854	0·1438	0·149
0·954	0·1371	0·153
1·054	0·1312	0·157
1·254	0·1214	0·163

(4) f = 1·936 ml./sec.; c = 0·00434M.

h (cm.).	r (cm.).	Surface age (sec.).
0	0·7471	0
0·050	0·5360	0·036
0·100	0·4500	0·058
0·150	0·3920	0·073
0·200	0·3430	0·084
0·300	0·2718	0·100
0·400	0·2339	0·111
0·500	0·2040	0·118
0·600	0·1841	0·124
0·700	0·1706	0·129
0·800	0·1587	0·133
0·900	0·1513	0·137
1·000	0·1449	0·141
1·100	0·1384	0·144
1·200	0·1338	0·147

TABLE III.

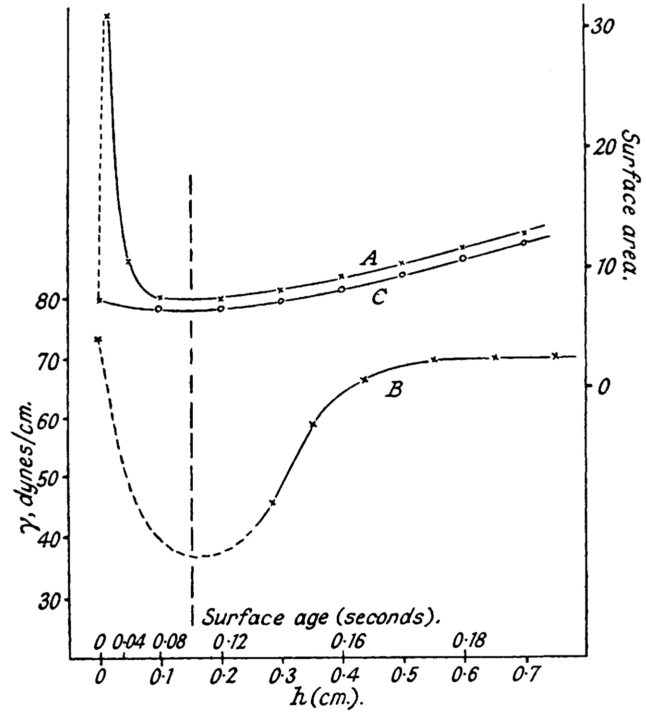
Sodium dodecyl sulphate solution.

Concn. = 0·00326M.; f = 1·555 ml./sec.

		Total energy of unit mass of liquid (ergs).				
		145	150	155	160	165
h (cm.).	r (cm.).	Calculated surface tension, dynes/cm.				
0·354	0·2400	71·3	69·1	66·8	64·6	62·3
0·554	0·1839	59·6	58·6	57·7	56·6	55·5
0·754	0·1522	59·6	58·8	58·1	57·2	56·4
0·954	0·1371	60·3	60·2	59·6	58·8	58·2
1·154	0·1260	63·1	62·5	61·9	61·3	60·6

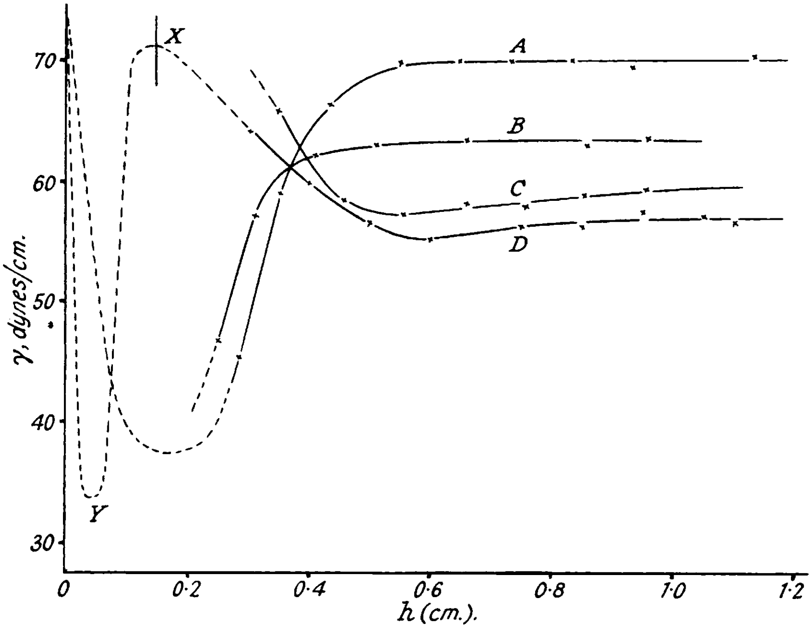
The surface tensions obtained for a 0·00109M-solution are plotted both against distance from the orifice, and against surface age, in Fig. 1 (full line *B*). If considerations of area change are excluded, it was to be expected that over the 0·1—0·2-second surface-age range the tensions should either decrease, or remain constant if adsorption was complete. In contrast, however, the tension values show a rapid rise over a tension range of at least 25 dynes/cm., followed by a steady tension value. Although the *h* axis in Fig. 1 extends only to 0·7 cm., this steady value has been found to persist down the jet as far as accurate tension measurement is possible, *i.e.*, to $h = 1{\cdot}5$ cm. For reasons explained in Parts X (*loc. cit.*) and XV (preceding paper), it is not possible to obtain accurate tension values in the *h* range below 0·25 cm. ; for example, the internal and external radii become equal, and thus the surface tension term vanishes, within the *h* range 0·1—0·2 cm. However, the surface tension of the solution at the instant the liquid leaves the orifice will be near to the water value, and must then fall rapidly to some value below the lowest recorded tension. Measurements of change in surface area (discussed below) would indicate that the portion of curve *B* which is experimentally inaccessible has the approximate shape indicated by the broken portion of the curve.

FIG. 1.



The surface tension of this solution was 62·8 dynes/cm. by the drop-weight method, and 58·0 dynes/cm. by the vertical-plate method, and the latter technique has been accepted as a method of recording the tension of the equilibrium, orientated surface film. The measured tensions recorded in Fig. 1, however, fall as low as 45 dynes/cm., and it appears probable that even lower values may occur nearer the orifice. It was considered that these low values might result from compression of the surface film at a rate greater than the rate of desorption, since it was already known (Part X, *loc. cit.*) that the surface area of the contracting jet undergoes an initial contraction, followed by a rapid expansion. The initial contraction which occurs in jets of pure water is insufficient to produce this effect. Curve *C* (Fig. 1) shows the area changes for a jet of water flowing at the same rate (1·256 ml./sec.) as that used for the alkyl sulphate solution ; the area per unit volume, originally 7·5, does not fall below 6·5 before expansion commences. The time axis in Fig. 1 applies to curves *A* and *B* only, and it is not possible from the information in Fig. 1 to derive rates of contraction for the water jet, but it is clear that, if the jet of alkyl sulphate solution undergoes similar area changes, the degree of contraction would be insufficient to influence appreciably the surface properties. The corresponding area–*h* curve for the solution was therefore determined accurately from the measured jet dimensions, and is shown as curve *A* in Fig. 1. This curve differs from the water curve *C* in that the surface area undergoes a considerable contraction (from 31 to 7 area units) within the first 0·1 cm. of jet. Although at the instant of its formation the surface will have almost the tension, and thus the direction, of pure water, it is not experimentally possible to carry out area measurements in this region (represented by the initial broken section of curve *A*). The area of unit volume of jet liquid may be expressed as $2/r \sin\theta$ (where θ is the angle of slope of the jet surface), and with the apparatus employed it was possible to view the jet within 0·01 cm. of the orifice. Within the *h* range 0·01—0·15 cm. the jet was found to undergo the rapid contraction shown by curve *A*, and the initial 0·01-cm. portion of the jet has no practical significance in this connection. The area reaches a minimum at $h = 0{\cdot}15$ cm., and increases thereafter.

FIG. 2.



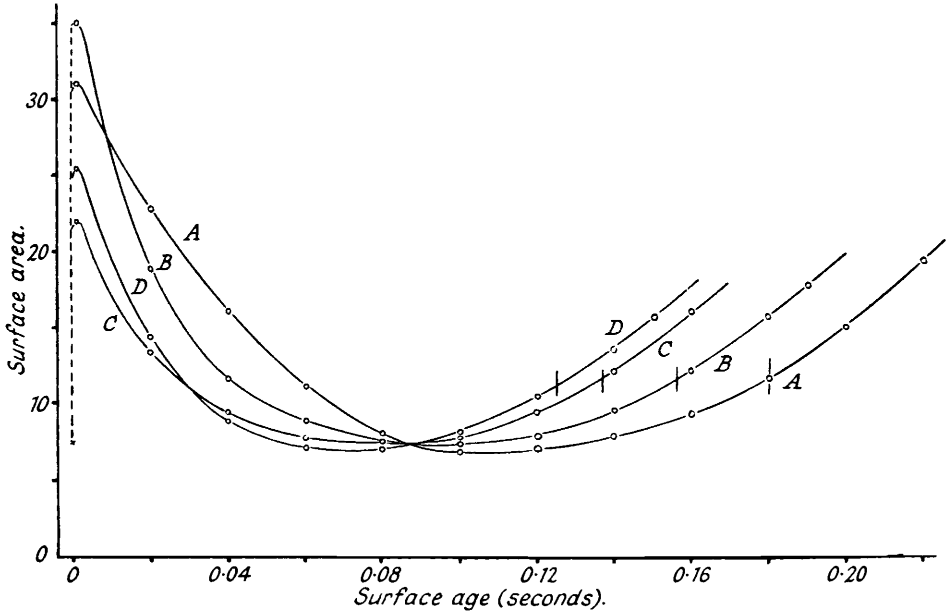
Curve.	*Concn.* (M. × 10³).	f, *ml./sec.*
A	1·09	1·256
B	2·17	1·335
C	3·26	1·555
D	4·34	1·936

The shape of the tension curve *B* can be related directly with the area curve *A*. As adsorption occurs the tension falls, and this accelerates contraction, until at the minimum of each curve the surface contains an amount of adsorbed material in excess of the equilibrium value. Surface expansion then occurs; although the rate of expansion (1 cm.² to 20 cm.² in 1 second) is much less than the initial contraction rate, it is greater than the rate at which the surface deficit can be replenished by adsorption, and the surface tension rises rapidly. As the surface excess diminishes, the rate of adsorption increases until a stage is reached (represented by the level portion of curve *B*) where the rate of decrease of surface concentration due to expansion equals the rate of increase due to adsorption.

The present results represent, so far as is known, the only direct measurement on rates of adsorption of long-chain alkyl sulphates to liquid surfaces. Since expansion rates are known with some accuracy, the rates of adsorption on to the expanding surfaces can be calculated, and from this the rate of adsorption on to stationary surfaces. It is hoped to discuss this process in more detail in a later paper.

Surface-tension and surface-area determinations similar to those given in Fig. 1 have been carried out on the other three jets whose dimensions are given in Table II, in order to assess the influence of bulk concentration on these effects. The range of concentrations enployed was below the critical concentration for micelle formation (0·0065M.), so that the surface properties of the films were not influenced by micelle formation in bulk solution. The variation in calculated surface tension along the jets is shown in Fig. 2, and the surface area is plotted against surface age in Fig. 3. At all concentrations steady values of tension are obtained along the jet surface beyond about 0·6 cm. from the orifice. In Fig. 3, the short vertical lines cutting the curves represent the surface ages corresponding to h = 0·6 cm. on each jet, and it is particularly significant that steady values of tension (Fig. 2) are obtained in each jet as soon as the rate of surface expansion becomes constant. It will be seen from Fig. 3 that the constant rate of surface expansion beyond h = 0·6 cm. is substantially the same for all jets. The steady tensions can therefore be interpreted readily as representing a balance between expansion and adsorption rates; the expansion rates are constant for all concentrations, but as the bulk concentration increases the rate of adsorption also increases, so that the steady surface-tension value is lowered correspondingly. It is of interest here to compare the surface-tension values given for the four solutions by the jet, the drop, and the vertical-plate method. These values are collected in Fig. 4. The region between the drop-weight and the vertical-plate curve represents the region within which surface tensions of equilibrium films disorientated to various extents will lie; tensions above the drop-weight curve can only be obtained at surfaces which are expanding at a rate in excess of the rate of adsorption. It is theoretically possible therefore to obtain tensions at any position between the drop-weight curve and the pure-water (broken line) value; the contracting-jet curve in Fig. 4 shows the extent to which this occurs with the expansion rates employed (Fig. 3).

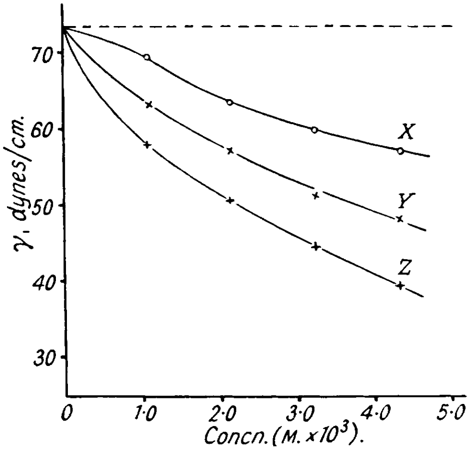
FIG. 3.



Curve.	*Concn.* (M. × 10^3).	f, *ml./sec.*
A	1·09	1·256
B	2·17	1·335
C	3·26	1·555
D	4·34	1·936

As the h value decreases below 0·6 cm., the tension falls rapidly in the case of the most dilute solution; curve *A* (Fig. 2) has already been considered with reference to Fig. 1. When the concentration is increased to 2·17 × 10^{-3}M. (curve *B*), the same shape of curve is maintained, but the fall in tension is not so rapid, since the steady tension is lower. Curve *B* can probably be extended to the orifice in a manner similar to curve *A*. However, when the concentration is increased further (curves *C* and *D*), the tension increases over the measurable h range below 0·6 cm., and an additional factor is clearly being introduced. The following tentative hypothesis is proposed as an interpretation of this effect. The measured tensions (curve *D*) can be extrapolated back to some point *X* having a tension near the water value. On the other hand, the initial fall in tension from the orifice in the case of the more concentrated solution *D* must be more rapid than for solution *A*, since the rates of compression (Fig. 3) are comparable while the rate of adsorption is greater. Therefore the surface tension of solution *D* must fall to some point *Y* (Fig. 2). It follows that within the very narrow *h* range between *X* and *Y* some feature must arise to restore the low surface tension rapidly to about the water value. When the bulk concentration is small (curve *A*, Fig. 2), the quantity of adsorbate on the surface may not be sufficient to produce, even after compression, a surface excess beyond the monolayer quantity. With higher concentrations, the monolayer may be produced before the end of the compression process. The rates of compression which obtain in the jet are probably too rapid for the normal desorption by diffusion from the surface to occur, and further rapid compression of the monolayer (at point *Y*) may give rise to the aggregation of adsorbed long-chain ions into micelles at the surface. It is already known that such aggregation is an extremely ready process in bulk solution, and it is believed (Powney and Addison, *Trans. Faraday Soc.*, **1937**, **33**, 1243) that ionic micelles have a negligible surface activity. This aggregation may account for the rapid rise of tension between *Y* and *X*. The vertical line at *X* represents the *h* value at which the surface area begins to expand. Thereafter the surface micelles may be considered to revert to single surface-active ions, with consequent fall in tension along the jet until the steady value is reached. Curve *C* may be interpreted in a similar way, and therefore the shape of the γ–h curves will depend on whether the initial adsorption and compression processes produce, on the surface, more or less than the monolayer quantity of adsorbed solute.

FIG. 4.



X, Contracting-jet method.
Y, Drop-weight method.
Z, Vertical-plate method.

Jets of Carbon Tetrachloride into Sodium Dodecyl Sulphate Solution.—The dynamic tensions at the surface of a jet of carbon tetrachloride flowing into an aqueous solution of sodium dodecyl sulphate have been studied in order to determine whether the features characteristic of liquid→air jets occurred also in the liquid→liquid system. The apparatus and technique used were precisely as described in Part XV (preceding paper) except that the water in the tank was replaced by the sodium dodecyl sulphate solution. In order that the results might be comparable, the orifice used was that employed in the liquid→air experiments described above. However, when this orifice was immersed in the aqueous solution, its lip was wetted preferentially by this solution, so that the jet of carbon tetrachloride flowed cleanly from the inside edge of the orifice (internal radius, 0·600 cm.). It was not possible to carry out experiments over the full concentration range employed for the liquid→air jets; because of the critical flow rate phenomenon discussed in Part X (*loc. cit.*), the low interfacial tensions obtained with the more concentrated solutions led to break-up of the jet. In order to obtain stable jets at these higher concentrations it would have been necessary to use flow rates above 10 ml./sec., which was not practicable.

Two jets have been measured, and their dimensions and surface ages are given in Table IV.

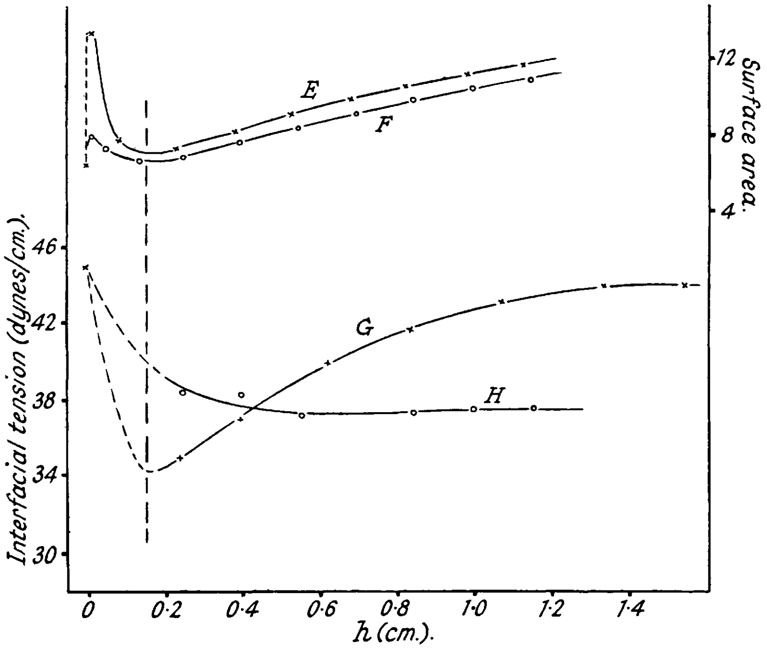
By use of the equation developed in Part XV (preceding paper), the interfacial tensions along these jets have been calculated, and are plotted against *h* in Fig. 5, which shows the corresponding area curves also. The concentrations employed are at the lower limit of the concentration range used in the liquid→air jets, and curves *G* and *H* (Fig. 5) are to be compared with curve *A* (Fig. 2) rather than with curve *D*. Owing to the less rapid narrowing which occurs with a liquid→liquid jet, the initial contraction in area, though quite definite, is less pronounced than in the case of the liquid→air jet. Comparison of curve *A* (Fig. 1) with curve *E* (Fig. 5) shows that the liquid→air jet area contracts from 31 to 7 area units, while the liquid→liquid jet contracts from 13 to 7 area units, in a similar time and distance. In consequence the initial fall in tension from the pure water interfacial tension value (curve *G*, Fig. 5) is not so pronounced. Thus the tension at the liquid→air jet (curve *B*, Fig. 1) fell to at least 13 dynes/cm. below the vertical-

TABLE IV.

Jet dimensions : carbon tetrachloride→sodium dodecyl sulphate solutions.

(1) f = 1·876 ml./sec.; c = 0·00075M.			(2) f = 2·504 ml./sec.; c = 0·0015M.		
h (cm.).	r (cm.).	Surface age (sec.).	h (cm.).	r (cm.).	Surface age (sec.).
0	0·6000	0	0	0·6000	0
0·088	0·4370	0·039	0·051	0·5085	0·021
0·238	0·3250	0·073	0·102	0·4395	0·034
0·388	0·2600	0·096	0·152	0·3915	0·045
0·538	0·2255	0·110	0·252	0·3285	0·061
0·688	0·2010	0·121	0·402	0·2760	0·078
0·838	0·1910	0·131	0·552	0·2420	0·090
0·988	0·1800	0·139	0·702	0·2215	0·101
1·138	0·1690	0·147	0·852	0·2040	0·109
1·338	0·1560	0·155	1·002	0·1925	0·117
			1·152	0·1835	0·123

FIG. 5.



Curve.	*Concn.* (M. × 10³).	f, *ml./sec.*
E *G*	0·75	1·876
F *H*	1·5	2·504

plate tension for that solution, whereas the lowest tension recorded by the liquid→liquid jet (curve *G*, Fig 5) does not fall to the vertical-plate value. The interfacial tension of the 0·00075M-solution measured against carbon tetrachloride by the drop-volume method was 33·5 dynes/cm. and the vertical-plate value is known to be several dynes/cm. below the drop-volume value. The lowest measured tension by the jet (curve *G*, Fig. 5) was 34·9 dynes/cm. Comparison of Figs. 1 and 5 will show that the rate of surface expansion in the liquid→liquid jet is not more than half the rate in the liquid→air jet. Therefore, although the shape of curve *G* (Fig. 5) resembles that of curve *B* (Fig. 1), the balance between expansion and adsorption is attained more slowly, and the steady value of tension is not reached until h = 1·5 cm.

The shape of the γ–h curves for liquid→air jets is a reflection of the initial rapid contraction of the surface. With liquid→liquid jets it was found possible almost to eliminate the initial area contraction by a small increase in flow rate. Curve *F* (Fig. 5) shows the change in area along a jet flowing at 2·504 ml./sec. If the rises in tension along the jet are, as has been presumed, a consequence of the initial area contraction, then the elimination of this contraction should also eliminate the upward drift in tension. Curve H (Fig. 5) shows the tension values corresponding to the area curve F, and it is significant that an upward drift in tension no longer occurs. In this jet, normal adsorption proceeds, and is influenced little by area changes, up to $h = 0{\cdot}2$ cm. Thereafter the curve H levels to a value (representing the balance between adsorption and surface expansion) of 37·5 dynes/cm. The surface tension of this solution, measured by the drop-volume method, was 25·5 dynes/cm.

Surface Tension at the Barrier.—It has been implied, in connection with Fig. 3, that, when the surface area of the jet begins to expand, the rate of expansion has a constant value through the remainder of the jet. This appears to be the case for that length of jet (up to about 1·5 cm. from the orifice) over which surface tensions can be determined accurately from jet dimensions. It would appear, however, that at greater distances from the orifice, where the jet assumes almost cylindrical form, the rate of surface expansion decreases. Thus the surface tension of the solution used to obtain curve G (Fig. 5) was determined at the barrier, 3·3 cm. from the orifice, by the wave method discussed in the following paper. A value of 32·5 dynes/cm. was obtained (cf. 33·5 dynes/cm. by the drop method), from which it may be inferred that the rate of surface expansion had decreased to a rate similar to that obtaining in the expanding drop.

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[*Received, July* 20*th*, 1950.]