115. *The Properties of Freshly Formed Surfaces. Part VI. The Influence of Temperature and Concentration on the Dynamic and Static Surface Tensions of Aqueous Decoic Acid Solutions.*

By C. C. ADDISON.

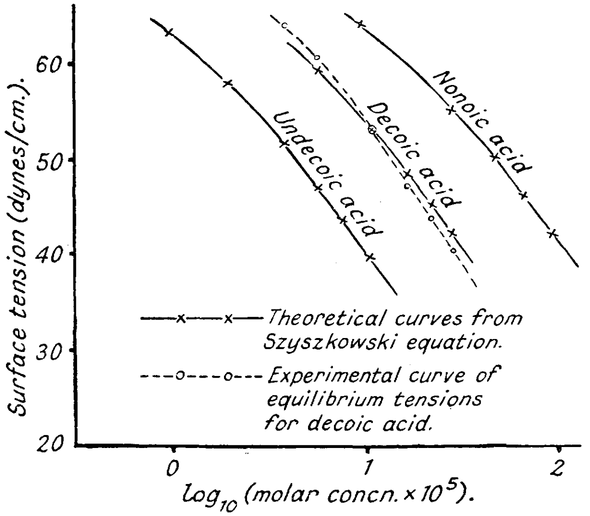
The solubility in water of decoic acid at 20° has been found by a surface tension method to be 0·0050%, and the static surface tension of the saturated solution is 40·2 dynes/cm. at 20°. The vibrating jet shows no appreciable fall in tension from the pure water value at any concentration, and a modified drop-weight method has been employed to measure the time required for the accumulation of the adsorbed layer of decoic acid. Diffusion has been found to proceed over periods from about 10 seconds up to several minutes depending on concentration. These times are greatly in excess of that normally attributed to the diffusion process, but are in accord with the times forecast by the general equation given in Part V. Diffusion equilibrium is followed by a very slow fall in the static surface tension. Measurements have been carried out over the temperature range 10—40°. Both dynamic and static surface tensions show an unusually large increase with temperature, particularly in the more dilute solutions, although the duration of the diffusion process is insensitive to temperature.

Since the fall in concentration in the surface layer of an expanding drop due to expansion of the surface cannot be replenished immediately by diffusion of decoic acid from the bulk, the tension varies with the rate of expansion of the drop. Temperature changes have a negligible effect on the tension at an expanding surface, in sharp contrast to the effect at a non-expanding surface.

THE vibrating jet studies reported in Parts I—IV (J., 1943, 535; 1944, 252, 477; 1945, 98) have established that for aqueous solutions of alcohols of chain length up to eight carbon atoms, the process of diffusion to the air-water surface is complete within 0·1 second for all concentrations except the most dilute, where the possible fall in tension from the pure water value is small. The minimum depth from which solute must be drawn to form the surface excess depends upon its solubility, which diminishes rapidly as chain length increases. This factor outweighs the increase in the velocity of migration of adsorbate to the surface, so that the time required for the establishment of diffusion equilibrium actually increases with chain length (Part IV, *loc. cit.*). An adsorption velocity–time equation was given in Part V (J., 1945, 354) which can be used to forecast this time where it lies outside the surface age range of the vibrating jet. Employing this equation, it appeared that if the solubility of the straight-chain alcohols of 10 carbon atoms and more was sufficient to give rise to an appreciable lowering of tension by a soluble film, the diffusion process would extend over minutes, and other experimental methods would then be available. Unfortunately, the solubility barrier restricts the study of the adsorption of the longer-chain alcohols. However, it is already known (Part IV, *loc. cit.*; Adam, "Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd Ed., p. 50) that, for static surfaces at least, the surface behaviour of primary alcohols and carboxylic acids is similar, and the slightly greater solubility conferred by the carboxyl group has enabled the decoic acid system to be studied experimentally. The order of time required for completion of diffusion has been recently reported (Addison, *Nature*, 1945, **156**, 600) and lies in the range calculated for *n*-decyl alcohol, so that the similarity in behaviour between the acids and alcohols extends to dynamic surfaces also.

The solubility of decoic acid has been found experimentally to be 0·0050% at 20°. At this concentration the static surface tension is 40·2 dynes/cm., yet the vibrating jet showed no appreciable fall in tension below the pure water value at surface ages up to 0·1 second. However, preliminary experiments with drops of the solution formed rapidly (in about 2 seconds) on a calibrated orifice showed that the subsequent time required for drops identical in size to fall away was accurately reproducible, and was a function of concentration and the drop weight. The method was therefore applied as described below. It has provided a means of studying changes in surface tension, clearly due to diffusion, by an entirely independent static method, and of comparing the conclusions with those reached employing the dynamic vibrating jet method. Again, the vibrating-jet technique cannot be readily adapted to investigation of the temperature effect in solutions, owing to the shortening of the jet which occurs at higher temperatures (Addison, *Phil. Mag.*, 1945, **36**, 73). With the present method it has been possible to measure dynamic and static surface tensions over the temperature range 10—40°.

FIG. 1.



EXPERIMENTAL.

The drop pipette used was similar to that described by Powney and Addison (*Trans. Faraday Soc.*, 1937, **33**, 1243) except that the air leak was replaced by a pressure screw. The liquid under test was maintained at the desired temperature by surrounding the reservoir bulb with a water jacket. It was found possible over the temperature range 10—40° to maintain the drop at the same temperature as the pipette liquid by surrounding it with an annular space filled with the liquid used for circulation through the water jacket. As the temperature coefficient of surface tension is large for decoic acid solutions, this temperature range was adequate. At temperatures above 40° the readings became erratic; this was probably due to evaporation of water from the drop surface rather than to temperature fluctuations.

Formation of Drop.—Liquid was forced from the jet by means of a pressure screw attached to the top of the pipette. Drops were brought to the desired size by observing their formation through a microscope fitted with an eyepiece scale. The tension when the drop fell away was determined from the drop weight, the correction factors of Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499) being used. In timing the drop life, a small drop was first formed on the orifice; this was brushed off by a piece of absorbent paper, leaving a fresh surface flush with the orifice, and the drop to be tested was immediately expelled. By this means the starting of the stopwatch could be made to coincide with the formation of a drop possessing a fresh surface, with an error not exceeding 2 seconds.

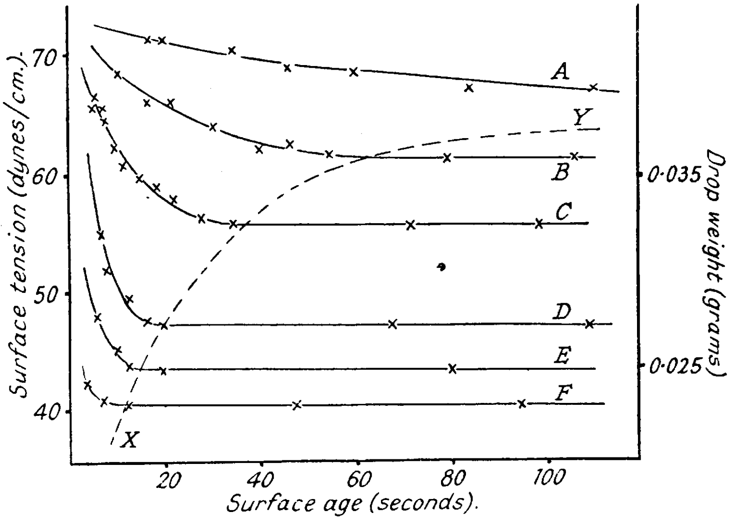
Purity of Decoic Acid.—In view of the high surface activity of any impurities of similar chain length which may be present with the decoic acid, a knowledge of the state of purity of the sample employed was of first importance. The material used was "*n*-capric acid" supplied by Messrs. B.D.H. Ltd., and had m. p. 30·2°. The acid was vacuum distilled and the distillate collected in eight separate fractions but no variation in m. p. or surface activity could be detected between the various fractions. The m. p. of the pure acid is given as 30° (Görgey, *Annalen*, 1848, **66**, 290), 31·3° (Krafft, *Ber.*, 1882, **15**, 1696) and 31·5° (Houben, *Ber.*, 1902, **35**, 3592). Although any impurities present were therefore in small proportion, the m. p. could not be accepted as a guarantee of adequate purity. As the main requirement in this work was that the surface tensions should be truly representative of the C_{10} acid, the theoretical curves relating surface tension (γ) and concentration (c) for acids of this order of chain length were calculated by using Szyszkowski's equation (*Z. physikal. Chem.*, 1908, **64**, 385), *viz.*, $\gamma/\gamma_0 = 1 - B \log (c/a + 1)$. The constant B is given by Szyszkowski as 0·411 for the straight-chain acids, and is independent of chain length. A similar value (0·407) has been reported for the straight-chain alcohols (Part IV, *loc. cit.*). The term a is constant for a given adsorbate, and is reduced by a constant factor for each additional carbon atom in the chain. The Szyszkowski values of a for the C_3—C_6 acids are tabulated below :

Carbon atoms in molecule (n).	a.	a_n/a_{n+1}.	Carbon atoms in molecule (n).	a.	a_n/a_{n+1}.
3	0·165	—	9	$11{\cdot}1 \times 10^{-5}$	3·38
4	0·051	3·24	10	$3{\cdot}30 \times 10^{-5}$	3·38
5	0·015	3·40	11	$0{\cdot}975 \times 10^{-5}$	3·38
6	0·0043	3·49			

Values of a determined for the straight-chain alcohols having 1—8 carbon atoms (Part IV, *loc. cit.*) have shown that though slight variations exist in a_n/a_{n+1}, the ratio shows no tendency to increase or decrease with chain length. The mean of the Szyszkowski values for a_n/a_{n+1} (3·38) was therefore employed to determine a for the longer chain lengths. By using the values for B and a thus obtained, the theoretical surface tension–concentration curves for the C_9—C_{11}

acids, nonoic, decoic and undecoic, were calculated, and are shown as full curves in Fig. 1. The equilibrium tension–concentration curve obtained experimentally with the sample used is superimposed as a broken line. The close agreement between the experimental and the theoretical decoic acid curve confirms the absence of other surface-active impurities, and of impurities capable of influencing the surface activity of the decoic acid.

FIG. 2.

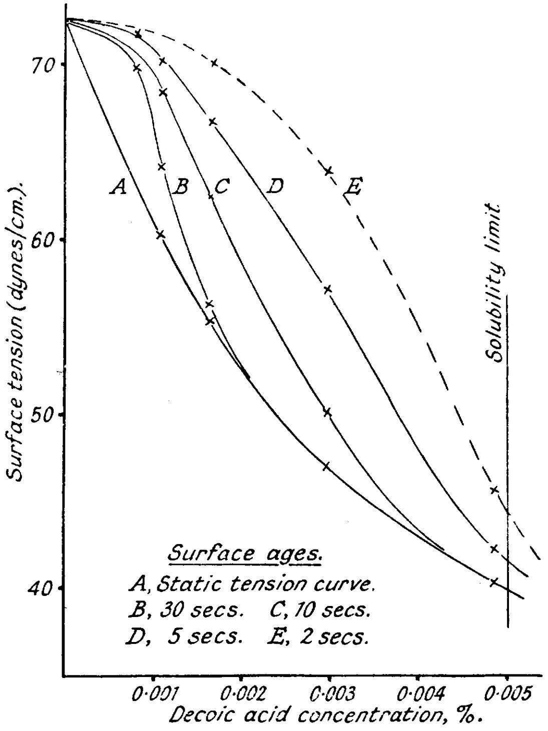


Decoic acid concentration, %.

A, 0·0008. B, 0·0011. C, 0·0017. D, 0·0030. E, 0·0042. F, 0·0049.

Solubility of Decoic Acid.—The very low solubility of decoic acid in water rendered difficult the preparation of standard solutions, since it was not possible to detect visually whether a trace of decoic acid added to a large volume of water had dissolved, or still adhered to the walls of the vessel. A modified form of the surface-tension technique used (Part IV, *loc. cit.*) for the slightly soluble alcohols was therefore employed. A saturated solution was prepared by adding excess decoic acid to 1 l. of water redistilled twice through Pyrex glass, warming it to 35° to melt the acid, swirling for one hour, and cooling again to 20°. A little of this solution was filtered, and the static surface tension corresponding to diffusion equilibrium (*i.e.*, the level portion of the γ–t curves, Fig. 2) was measured. The solution was then left in contact with decoic acid for 24 hours at 20°, and the static surface tension again measured to confirm saturation. The result obtained was 40·2 dynes/cm. at 20°. Solutions were then prepared by adding known amounts of the acid to 1 l. of water, and dissolving them at 35°. The γ–t curve was then obtained, and a solution giving a static tension higher than 40·2 dynes/cm. could be regarded as standard. A number of such solutions were so tested, and the static surface tension plotted against the concentration (curve *A*, Fig. 3). Extrapolation of this curve to 40·2 dynes/cm. gave the solubility of decoic acid in water at 20° as 0·0050%. Further standard solutions could then be made up conveniently from the saturated solution by dilution. Measurements were normally made on solutions freshly made up, but check tests on solutions kept for up to six days showed no ageing effects.

FIG. 3.



RESULTS AND DISCUSSION.

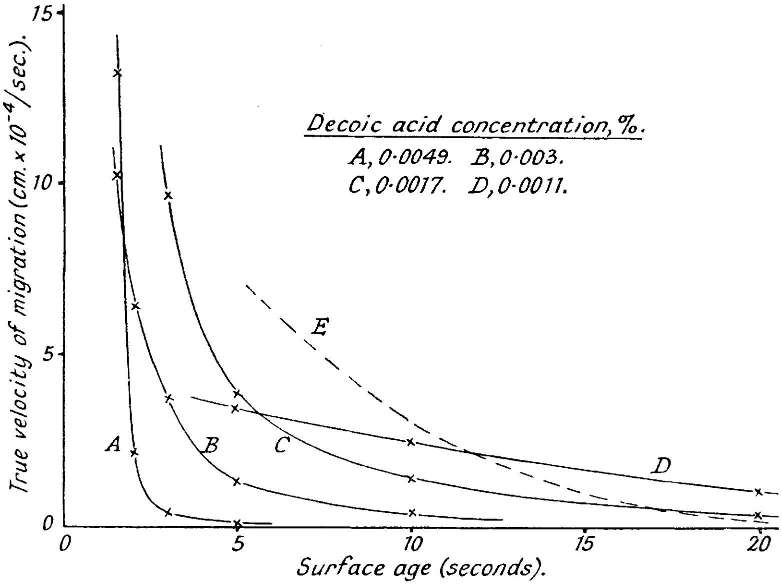
Surface Tension–Time Curves.—The results obtained at 20° are recorded in Fig. 2. The vertical axes show the drop weights measured as well as the surface tension, so that the order of experimental error is clear from the curves. Drop weights were accurate to the fourth place of decimals, and the error in this direction is negligible. The slight displacement of the points from an ideal curve is probably due to errors in timing the drop life, since up to 2 seconds were required for drop formation. Also, during these 2 seconds the surface is expanding rapidly, and little accumulation of adsorbate can occur at the surface. However, it is clear from the experimental results that the position of the surface tension–time curve for any particular concentration can be fixed with accuracy, and that owing to the high surface activity of decoic acid, small changes in concentration produce large changes in dynamic as well as static tension. Each curve consists of an initial fall from the pure water value (which is more rapid as concentration increases, but can be followed satisfactorily almost up to the solubility limit), followed by a very slow fall beyond the broken line *XY*. This slow fall is probably due to rearrangements in the established surface layer of the type known for other long-chain adsorbates (Alexander, *Trans. Faraday Soc.*, **1941**, **37**, 15; and references therein to earlier work). This drift, which was not of direct interest in the present experiments, was not studied in detail, and over the range of time recorded in Fig. 2 this slow fall in tension can be ignored.

It is of interest to compare the duration of the diffusion process found experimentally with that forecast by the general equation

$$v = a^n t e^{-akt} \qquad (1)$$

relating adsorption velocity (v) and time (t), developed in Part V for the straight-chain alcohols. This equation was deduced from vibrating-jet measurements, where there is no doubt that the tension changes are due solely to accumulation of adsorbate at the surface by diffusion from bulk. The shorter-chain carboxylic acids have not been studied by the vibrating jet in similar detail, but sufficient preliminary experiments have been conducted to confirm that the velocity of migration of acid molecules to the surface is of the same order as the reported values for primary alcohols of identical chain length. Whereas diffusion is complete for *n*-octyl alcohol within 0·1 second, the substitution of the appropriate decyl alcohol values for the constants a, k and n (obtained by extrapolation of the C_5 to C_8 values given in Part V) into equation (1) indicates that diffusion to the surface for *n*-decyl alcohol should require 22 seconds for completion in 0·0011% solution, and 12 seconds in 0·002% solution. The substitution of the carboxyl group renders the molecule rather more hydrophilic, thus increasing the solubility and reducing the velocity of migration to the surface. It was therefore to be anticipated that the time for establishment of diffusion equilibrium in the case of decoic acid would be rather greater than that forecast by equation (1); it can be deduced from Fig. 2 that the values for these concentrations are 64 and 30 seconds respectively. This agreement between the order of results obtained and those anticipated on diffusion theory supports the belief that the initial fall in tension (Fig. 2) is the result of diffusion to the surface. The broken line *XY* thus traces the boundary between dynamic and static surface tensions. The surface tension of the 0·0008% solution reached a static value of 63·5 dynes/cm. after about 6 minutes.

FIG. 4.



Dynamic tensions obtained from vibrating-jet measurements have been reported in Parts II—IV as tension–concentration curves, and the results from the present work at 20° have been collected in a similar form in Fig. 3 for comparison. The " equilibrium " curve *A* is a plot of the tensions obtained immediately after diffusion to the surface was complete. Static tensions at higher surface ages (not considered in detail here) would lie below the line *A*; the dynamic tension curves above line *A* resemble closely in form those reported in Parts II—IV. The broken curve *E* represents the probable position of the 2-second curve, as indicated by the extrapolation of the γ–t curves (Fig. 2) towards 72·8 dynes/cm. at zero surface age.

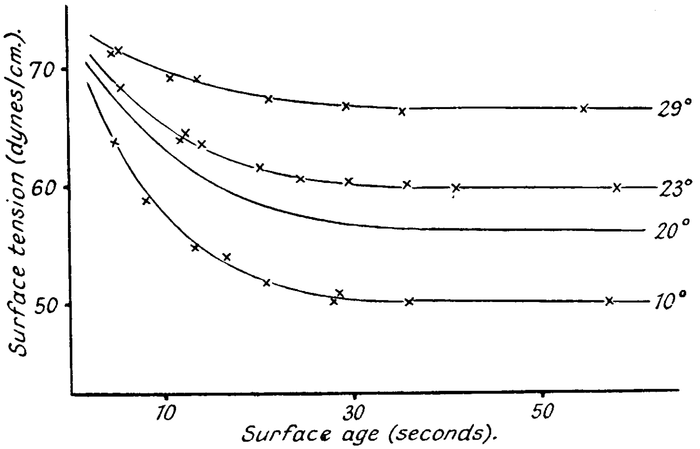
Migrational Velocity.—It was shown experimentally in Part IV for the amyl—octyl alcohols that over the available concentration range, $d\gamma/dc$ (as determined from the slope of the equilibrium curve *A*, Fig. 3) was approximately proportional to the time t_1 required for the establishment of diffusion equilibrium, and thus the *mean* velocity of migration of adsorbate molecules (V), determined from $V = -100M(d\gamma/dc)/KTt_1$, was constant. It was deduced theoretically in Part V that if experiments could be carried out at sufficiently high dilution, the value of V would fall with decreasing concentration, and that this effect would be more pronounced as chain length increased. The latter conditions are satisfied by the decoic acid system, and the values of V given below show the expected fall with dilution.

c, %.	$d\gamma/dc$.	t, secs.	$V \times 10^4$, cm./sec.	c, %.	$d\gamma/dc$.	t, secs.	$V \times 10^4$, cm./sec.
0·0011	9500	64	1·05	0·0030	4600	20	1·62
0·0017	7200	37	1·37	0·0049	3000	12	1·77

The decoic acid system therefore falls beyond the range of applicability of the migrational velocity term, and the values of V in this table cannot be accepted as representative of decoic acid for comparison with the alcohols.

True Velocity of Migration.—The adsorption mechanism given in Part V has been used to determine the true velocity of migration of decoic acid molecules to the surface at 20° and at four concentrations, and the velocity–time curves are given in Fig. 4. With the practical technique used it was not possible to obtain the peaks of the curves, but the die-away sections available are clearly part of a family of v–t curves resembling those recorded in Part V, and can be represented by equation (1); n and k are functions of chain length only, and a is proportional to the concentration c at high dilution. Attempts to reproduce the experimental curves by assuming n, k or a to have exactly the alcohol value were unsuccessful, indicating that the polar group has an influence on the manner of variation of n and k with chain length as well as on the ratio a/c. For example, the broken curve E (Fig. 4) is the theoretical v–t curve for n-decyl alcohol in 0·0011% solution, and is shown for comparison with curve D, deduced from experimental results on a decoic acid solution of the same concentration. The general agreement is satisfactory, but the slight increase in hydrophilic nature due to the carboxyl group is reflected in curve D in a lower velocity of migration at low surface ages, and the greater time required for the curve to reach zero velocity, *i.e.*, completion of diffusion.

FIG. 5.



Decoic acid concentration 0·0017%.

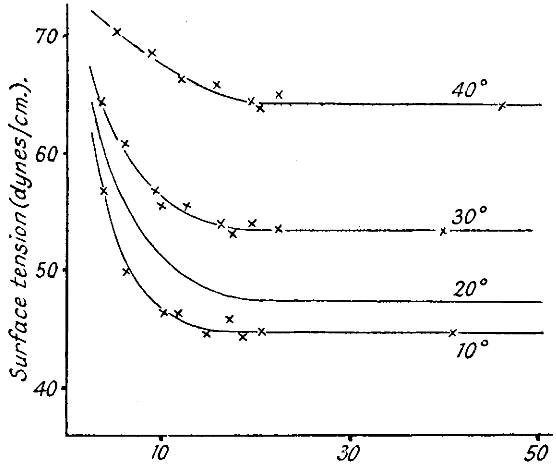
Influence of Temperature on Static and Dynamic Tensions.—Surface tension–surface age curves in the range 10—40° have been obtained experimentally for three concentrations, and are shown in Figs. 5—7. At a concentration of 0·0042% (Fig. 7) measurements were not made below 20° because of the danger of exceeding the solubility of decoic acid; some experiments at 10° gave erratic and high surface tensions, probably due to separation of decoic acid from solution.

Two general conclusions are apparent from each set of graphs : (*a*) relatively small changes in temperature have a profound effect on both static and dynamic tensions, and (*b*) change in temperature has little effect on the time required for the establishment of diffusion equilibrium.

Considering (*a*), the temperature coefficient increases with dilution. In a 0·0017% solution the mean temperature coefficient is approximately 1 dyne/cm. per degree, and is in marked contrast with the values not exceeding 0·1 dyne/cm. per degree found (Powney and Addison, *loc. cit.*) for sodium dodecyl sulphate solutions, and with the commonly accepted order of values for both solutions and pure liquids. In 0·003% concentration the coefficient is only a little less, and the tension again approaches the pure water value at the higher temperatures. Although it is generally accepted in the case of solutions that increase in temperature results in a decrease in adsorption and a consequent increase in the surface tension, it appears most improbable that relatively small temperature increases of this order can almost completely inhibit the process of adsorption; on the other hand, the increase in the kinetic agitation of the surface molecules may be sufficient to prevent orientation of the surface excess of decoic acid at both dynamic and static surfaces, and may thus prevent the surface excess being fully reflected in the surface tension. It is also significant that at a concentration of 0·0042% the temperature coefficient is less, and a temperature–tension curve derived from Fig. 7 indicates that the tension will not reach the water value at higher temperatures.

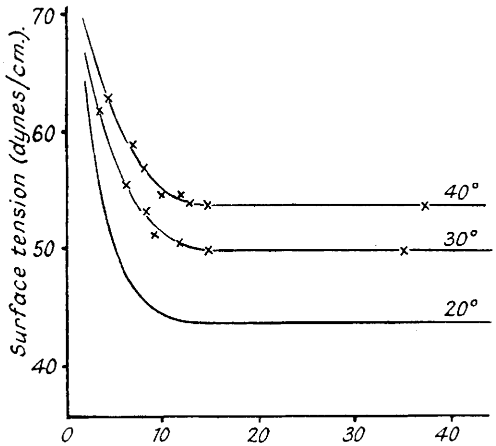
Considering (*b*), two opposing factors may operate in these systems. First, the rate of accumulation of adsorbate at the surface was shown in Part III (*loc. cit.*) to be proportional to the free surface energy as defined by $\gamma_t - \gamma_E$, where γ_t is the dynamic tension at time t, and γ_E is the static value. γ_E for decoic acid increases rapidly with rising temperature, and therefore the free surface energy, the rate of accumulation of adsorbate, and the velocity of migration to the surface (v) should all decrease as the temperature rises. Secondly, if the high static tensions at the higher temperatures can be taken to indicate a correspondingly small surface excess of decoic acid, the depth d from which adsorbate is drawn should also decrease with rising temperature. Since the time t_1 required to build up the surface layer is a function of the ratio d/v, then proportionate alteration of d and v with increasing temperature provides a satisfactory explanation of the constancy of t_1 in the case of the 0·0042% solution. However, the application of this reasoning to the lower concentrations involves the doubtful assumption that at higher temperatures little surface excess exists, and it is probable that a more complex mechanism operates. The influence of temperature changes on the surface tension of solutions has received but little attention, particularly at high dilutions, and it is proposed to investigate this aspect further.

FIG. 6.



Decoic acid concentration 0·003%.

FIG. 7.



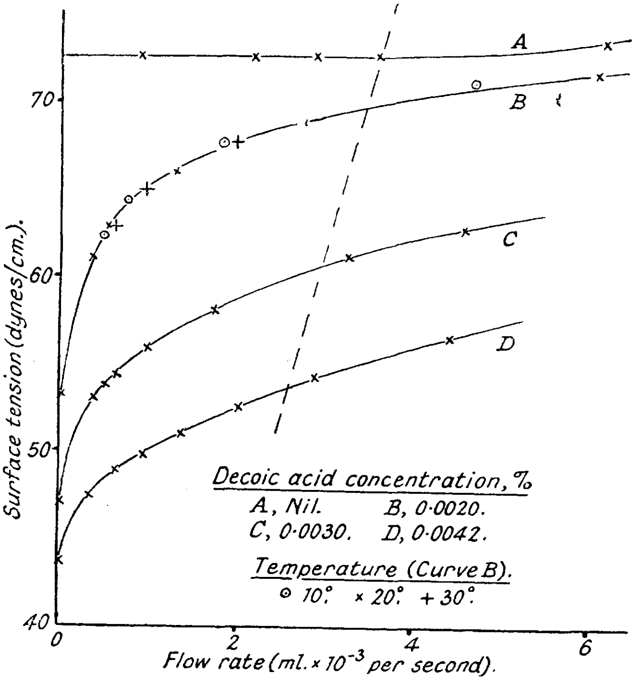
Decoic acid concentration 0·0042%.

Adsorption to an Expanding Surface.—It has already been verified for solutions of dyestuffs (Gibby and Addison, J., 1936, 119) and for soaps and long-chain alkyl sulphates (Powney and Addison, *Trans. Faraday Soc.*, 1938, **34**, 356) that in drop-weight measurements, if 12 seconds be allowed for the formation of each drop, mechanical errors are eliminated. It is clear that with these solutes, the constant decrease in surface concentration due to expansion of the surface must be almost immediately replenished by diffusion from the bulk. With the decoic acid solutions discussed above, diffusion continues for so long that the drop-weight method as frequently employed in stalagmometry (*i.e.*, slow formation of drop until the drop weight is equivalent to the surface tension) cannot be used. The apparatus was adapted for these experiments by replacing the pressure screw by an air leak formed from a piece of capillary glass tubing drawn out to a fine thread which could be broken off to give the required rate of expansion of drop. The experimental results obtained for three concentrations are tabulated below, and the flow rate calculated therefrom is plotted against the surface tension in Fig. 8. It should be emphasised that this tension value has no direct significance in terms of either static or dynamic tensions in the sense in which these terms are used earlier in this paper.

Concn., %.	Temp.	Drop weight, mg.	Secs. per drop.	Concn., %.	Temp.	Drop weight, mg.	Secs. per drop.
Pure water	20°	43·3	50, 20, 15, and 12	0·0030	20°	31·0	80
,,	,,	43·7	7	,,	,,	31·4	60
,,	,,	44·3	3	,,	,,	31·7	48
0·0020	10	36·7	75	,,	,,	32·5	32
,,	,,	37·8	50	,,	,,	34·8	20
,,	,,	40·1	22	,,	,,	36·0	11
,,	,,	42·3	9	,,	,,	37·0	8
,,	20	35·9	100	,,	,,	39·8	5
,,	,,	37·0	72	0·0042	20	27·5	80
,,	,,	38·0	44	,,	,,	28·4	44
,,	,,	39·0	30	,,	,,	28·9	31
,,	,,	40·9	15	,,	,,	29·6	21
,,	,,	42·6	7	,,	,,	30·6	15
,,	30	37·0	60	,,	,,	31·8	11
,,	,,	38·4	40	,,	,,	33·2	7·5
,,	,,	40·0	20				

The broken line in Fig. 8 represents the flow rate corresponding to 12 seconds per drop. It will be seen from the pure water curve that a small mechanical error is introduced at higher flow rates, and the apparent slight increase in tension due thereto will be present in the curves for the decoic acid solutions also. The significant range is therefore that which lies between the broken line and zero flow rate, and in no case is the surface tension independent of flow rate. The tension values recorded in Fig. 8 for zero flow rate are the static values already determined for these concentrations, and clearly form the limiting points for the expanding drop curves. The surface tensions obtained by this technique are the resultant of two factors, *i.e.*, the accumulation of a surface excess of decoic acid due to diffusion from the bulk solution, and the diminution of the surface concentration by expansion of the surface. At the higher flow rates, much of the acid diffusing to any given unit area of surface will be removed from that unit area by expansion; the surface concentration will be maintained at a low level, and the surface tension will be correspondingly high. As the flow rate (which is an index of the rate of expansion of the surface) decreases, the surface is able to maintain a higher concentration of adsorbate, and the surface tension decreases accordingly, until at zero flow rate it is equivalent to the static tension. Each curve was obtained at 20°, but points on the 0·0020% curve have also been determined at 10° and 30°. It is of interest that the latter points lie, within experimental error, exactly on the 20° curve. In view of the large temperature coefficient found for non-expanding surfaces, it appears that the power of an adsorbed decoic acid layer to lower surface tension is altered fundamentally by expansion of the surface, and the quantitative study of adsorption to expanding surfaces will form the subject of a later communication.

FIG. 8.



HARRIS INSTITUTE TECHNICAL COLLEGE, PRESTON.
UNIVERSITY COLLEGE, NOTTINGHAM.

[*Received, November 26th*, 1945.]