

709. *The Properties of Freshly Formed Surfaces. Part XII. An Experimental Study of the Desorption Process with Particular Reference to Aqueous Decyl Alcohol Solutions.*

By C. C. ADDISON and S. K. HUTCHINSON.

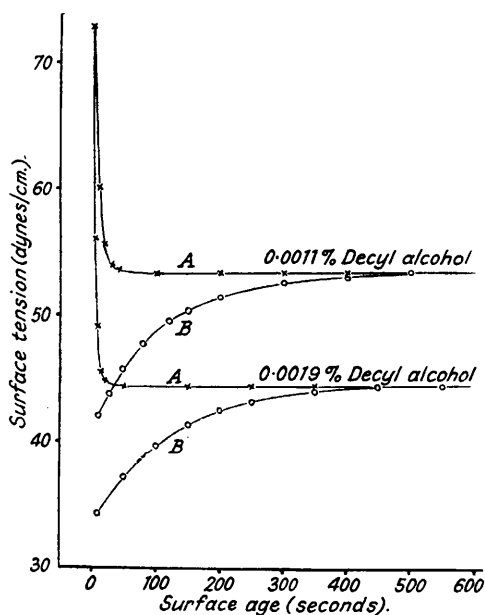
Desorption from soluble films of decyl alcohol has been found to be sufficiently slow to be measurable by the vertical-plate technique. An excess of alcohol in the film, beyond the equilibrium value, has been obtained by two methods: (*a*) by pouring the solution into a trough having small surface area, and (*b*) by spreading a film of decyl alcohol on the surface. Desorption rates have been found to depend on surface excess and temperature rather than on the bulk concentration of solute. As chain length decreases, the desorption rates increase; at chain lengths below C<sub>7</sub>, desorption is too rapid to be measurable by these techniques. The sensitivity of desorption rates of decyl alcohol to temperature is probably responsible for a unique change in the sign of the temperature coefficient which is observed with the equilibrium surface tensions.

In the studies of rates of adsorption by the vertical-plate method (Part XI, preceding paper) the surface was invariably swept by means of a waxed barrier immediately before the vertical plate was applied to the surface. Under these conditions the surface tension fell from the water value to the equilibrium value. However, it was observed that when an aqueous solution of decyl alcohol having the equilibrium surface tension was poured into the trough, and the vertical plate applied immediately to the unswept surface, the initial tension was below the equilibrium value by as much as 10 dynes/cm. The tension then increased to the equilibrium value during about 500 seconds at room temperature. Since care was taken to ensure that the surfaces were free from contamination, the pouring of the solution from one vessel into another was clearly responsible for the initial low tensions. (Fig. 1 shows typical results obtained at 20° for two concentrations, at the swept and the unswept surfaces.) The upward drifts in tension were reproducible and were considered to be sufficiently unusual to merit fuller investigation. Since the initial surface tension at an unswept surface is lower than the equilibrium value, the surface must contain an amount of decyl alcohol greater than the equilibrium surface excess. In the process of pouring a decyl alcohol solution from its containing vessel into the trough a large surface area is created. This area is then, in effect, reduced to the surface area of the trough, and if the desorption of decyl alcohol is sufficiently slow this pouring process could result in an over-

crowding of the alcohol molecules on the surface of the solution in the trough. The subsequent upward drift in tension would then reflect the desorption of that quantity of decyl alcohol in excess of the equilibrium value. On this basis decyl alcohol solutions would represent an ideal system for quantitative studies of the desorption process, in view of the readily measurable rates of desorption involved. The following preliminary experiments were carried out in an attempt to confirm the above interpretation.

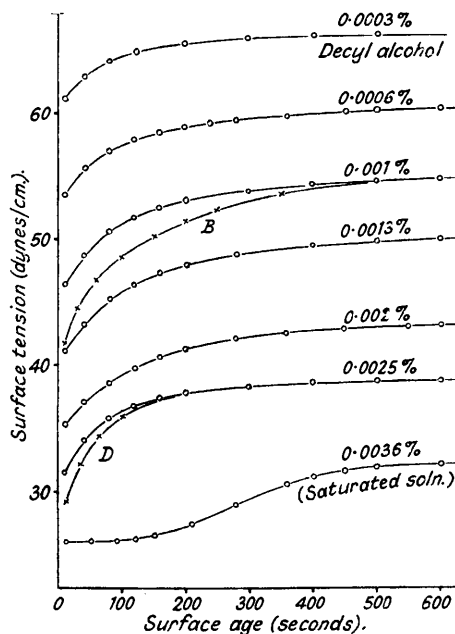
(1) *Influence of Surface Area of Trough.*—Fig. 2 shows upward drifts in tension obtained for unswept surfaces at 20° over a range of concentration. With the exception of curves B and D all the curves were obtained by using a trough which gave a liquid surface area of 78.5 cm.<sup>2</sup>. In each experiment the trough was filled in about 15 seconds by pouring the solution (675 ml.) at a uniform rate from the same 1-l. flask. Curves B and D were obtained by employing an identical experimental technique except that the troughs had a smaller liquid surface area. As expected, decrease in surface area of the trough resulted in a further fall in the initial tension, but the equilibrium value to which the tension ultimately drifted was independent of surface area.

FIG. 1.



Curves A: Swept surface.  
 " B: Unswept surface.  
 Surface area of trough, 64.3 cm.<sup>2</sup>.

FIG. 2.



Surface area of trough:  
 B, 38.0 cm.<sup>2</sup>. D, 64.3 cm.<sup>2</sup>.  
 Other curves, 78.5 cm.<sup>2</sup>.

(2) *Partitioning of the Trough.*—The rectangular trough was divided into two equal chambers by means of a vertical waxed glass partition which reached to within 0.5 cm. of the bottom of the trough. Thus the only way by which liquid could pass from one chamber to the other was through the narrow space beneath the partition. Solution was then added to the trough until the bottom of the partition was just covered. This required only a few ml., and the surface was then in two distinct and unconnected portions. These surfaces were allowed to stand until the equilibrium surface tension was reached. The trough was then filled to the requisite level by pouring the solution into one chamber only. Of the two surfaces thus formed, the one through which the solution had been poured was expected to show molecular overcrowding and thus a low surface tension, while by the same reasoning the tension at the other surface should not have deviated from the equilibrium value. Measurement of the tension at the two surfaces immediately after pouring was complete confirmed that this was the case.

(3) *Influence of Surface Bubbles.*—During the pouring of the decyl alcohol solution into the trough any bubbles formed on the surface broke almost immediately. When decyl alcohol was dissolved in *N*-sodium hydroxide solution, any bubbles formed were found to be much more persistent, and to have a marked effect on the surface properties of the film. The effect is

illustrated in Fig. 3. In the absence of surface bubbles, solutions of decyl alcohol in *N*-sodium hydroxide showed an upward drift (Curve *B*) but the equilibrium surface tension was lower (cf. Curve *A*) than in the case of the aqueous solution. This lower tension is probably to be associated with the reduced solubility of decyl alcohol in sodium hydroxide solutions. When the surface was partly covered by bubbles (although no bubbles were in contact with the vertical plate) the upward drift was almost completely eliminated and the surface tension remained at an approximately constant value over the measured time range (Curve *C*). This may be explained by considering that any decrease in surface excess at the bubble-free surface which occurs as a result of desorption is replenished by the decyl alcohol which is adsorbed at the bubble surfaces and thus is out of direct contact with the bulk of the solution.

The above preliminary experiments and the more detailed measurements given below have confirmed that when a decyl alcohol solution is poured from one vessel into another, the molecules adsorbed at the new surface so created are overcrowded as a result of their slow rate of desorption, and that this simple pouring process is therefore equivalent to compression of the surface film. It is noteworthy that when an aqueous solution of sodium dodecyl sulphate was allowed to fall through an oil layer, Alexander (*Trans. Faraday Soc.*, 1941, **37**, 15) observed that the initial interfacial tension was a few dynes less than the equilibrium value; this was attributed to "an initial interfacial overcrowding by the adsorbed molecules liberated when the unstable emulsion drops coalesce."

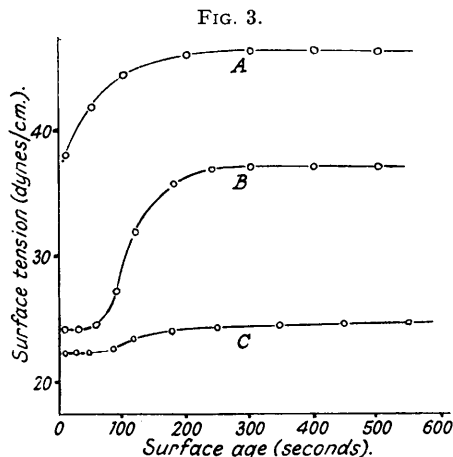
No experimental study of the desorption process in alcohol-water systems has yet been made. Because of the experimental simplicity of the "compression-by-pouring" technique it has been used to explore the influence of concentration, temperature, and chain length on rates of desorption, and the results are discussed below.

**Concentration.**—Tension-time curves at 20° have already been given in Fig. 2. The upward drifts which are obtained over the full concentration range are similar in magnitude; desorption requires about 500 seconds for completion, and this time is almost independent of concentration. Below about 0.0025% concentration the initial tensions do not fall below the uncompressed monolayer value of 32.5 dynes/cm. At higher concentrations the initial tensions are below this value; for these solutions, which are not saturated, compression of a monolayer or near-monolayer results in very rapid desorption (see below) so that the tension does not remain, except for a brief interval of time, below the monolayer value of 32.5 dynes/cm. However, when a saturated solution of decyl alcohol is poured into the trough the monolayer already present will be further compressed. Although this will involve the introduction into the monolayer of few additional molecules, the increase in surface pressure may well be appreciable. These additional molecules in the surface will not remove the bulk concentration far from the saturation value, and in consequence desorption will be slow. Thus the initial low value of surface tension (26 dynes/cm.) is maintained for about 150 seconds and the tension thereafter drifts to the value equivalent to the uncompressed monolayer. This drift represents the transfer of those molecules which are in excess of the uncompressed monolayer, from the surface into bulk solution to restore saturation.

Support for the above interpretation is provided by measurements carried out over a narrow temperature range on a decyl alcohol solution saturated at 20° (Fig. 4). When the temperature is increased above 20° the concentration is then below the saturation value. In consequence, the rate of desorption from the compressed monolayer is increased, and the initial period of constant tension is diminished, until at 27.5° the curve given by this solution is similar in shape to the curves shown in Fig. 2 for unsaturated solutions at 20°.

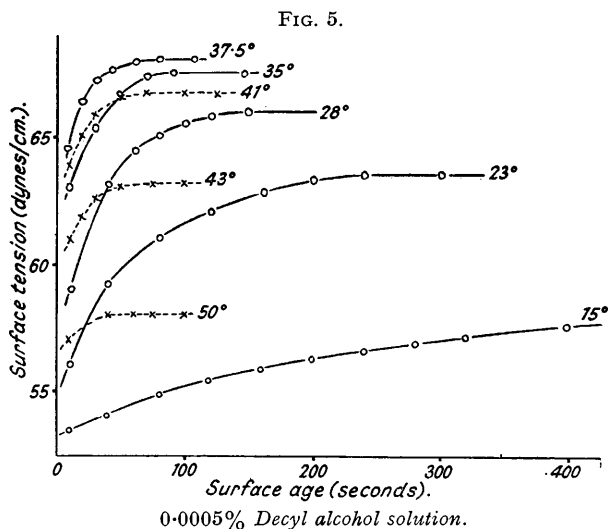
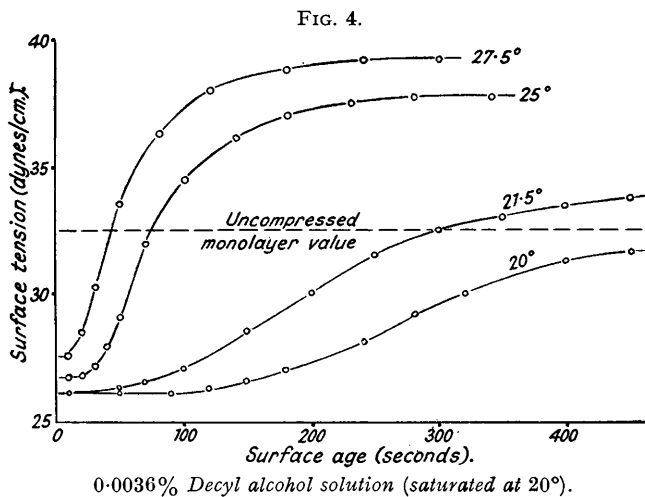
**Temperature.**—Desorption curves obtained within the temperature range 15–55° are given, for three separate concentrations, in Figs. 5–7. Similar sets of curves were obtained for several other concentrations, and in each set the following features are evident.

(a) The time taken to reach equilibrium tension diminishes rapidly with increasing temper-

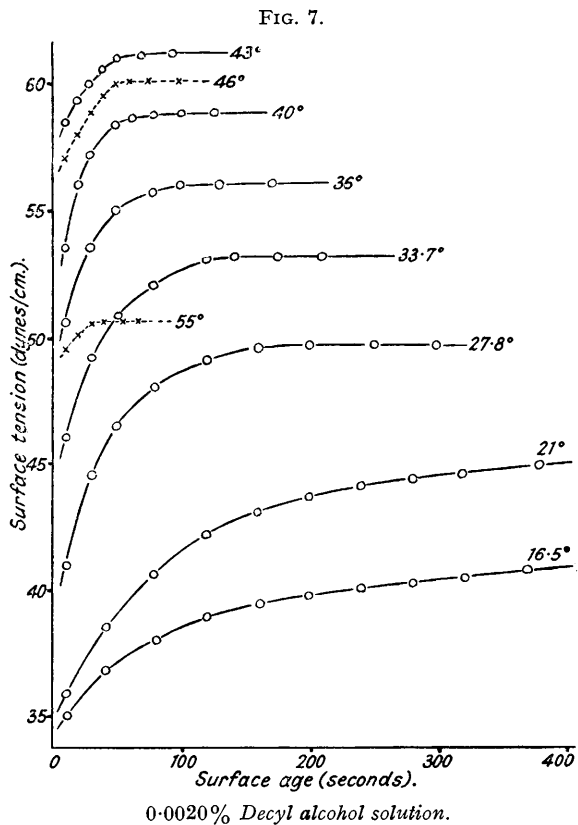
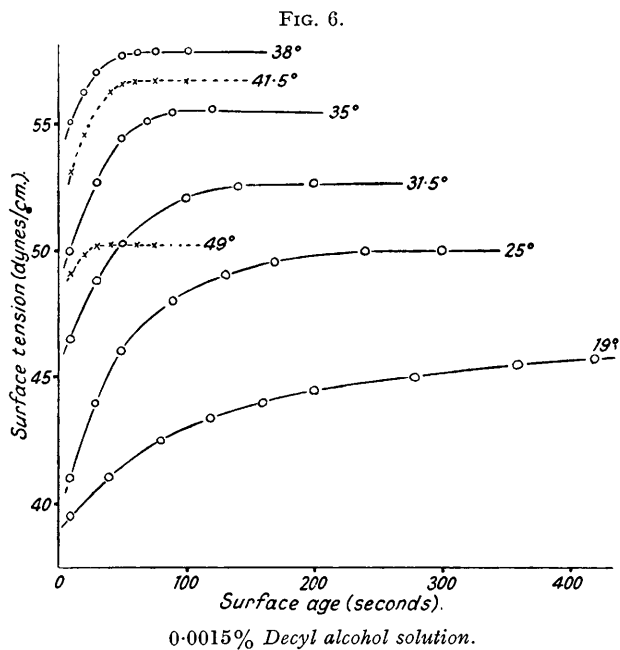


Curve A : 0.002% Decyl alcohol alone (23°).  
 B : 0.002% Decyl alcohol in *N*-sodium hydroxide ; no surface bubbles.  
 C : 0.002% Decyl alcohol in *N*-sodium hydroxide ; approx. 30% of surface carrying bubbles.

ature, indicating that the rate of desorption of decyl alcohol from the surface is extremely sensitive to temperature changes. For example, the period of 500 seconds which decyl alcohol solutions require to reach surface equilibrium at 20° is reduced to about 30 seconds at 50°. On the other hand, adsorption rates are little influenced by temperature changes (see, *e.g.*, decic acid measurements given in Part VI, *J.*, 1946, 579). These differences may be suitably explained on the assumption that the energy barrier to desorption (as well as to adsorption) is purely kinetic in nature. It may be calculated from experimental evidence such as that given in Fig. 1 that if the surface excess is deficient by an amount  $-\Delta\Gamma = 2 \times 10^{-8}$  g./cm.<sup>2</sup> below the equilibrium value, the adsorption process in a solution of 0.0011% concentration requires



23 seconds to restore equilibrium, whereas if the surface contains an amount  $+\Delta\Gamma = 2 \times 10^{-8}$  g./cm.<sup>2</sup> above the equilibrium value, the desorption process requires 450 seconds to restore equilibrium. It is clear from this example, chosen at random, that the energy barrier to desorption is large compared with the energy barrier to adsorption. During adsorption, a given small change in temperature will cause a slight shift in the energy distribution curve of the dissolved molecules, but will not make any considerable difference to the proportion of these molecules having kinetic energy above the barrier value. On the other hand, the kinetic energy of molecules of decyl alcohol adsorbed in a surface film may be regarded as being reduced, partly as a result of lateral adhesion, to a value below that possessed by corresponding molecules at the



same temperature in bulk solution. By increasing molecular agitation, an increase in temperature reduces the effect of lateral adhesive forces and thus raises the kinetic energy of a larger proportion of the alcohol molecules above the barrier value.

(b) Increase in temperature gives rise in the first place to an increase in tension. At a certain temperature the sign of the temperature coefficient is reversed sharply and beyond this temperature the tension falls regularly. In Figs. 5—7 the desorption curves obtained at temperatures where the temperature coefficient is positive are shown by full lines; beyond the inversion temperature the curves are shown, for clarity, by broken lines.

(c) Both positive and negative temperature coefficients are of the order of 0.5—1.0 dyne/cm. per degree. This coefficient is in agreement with the values determined for decolic acid solutions (Part VI, *loc. cit.*) but is again considerably in excess of the order of values (0.1 dyne/cm. per degree) for solutions of long-chain electrolytes (Powney and Addison, *Trans. Faraday Soc.*, 1937, 33, 1243) or short-chain compounds.

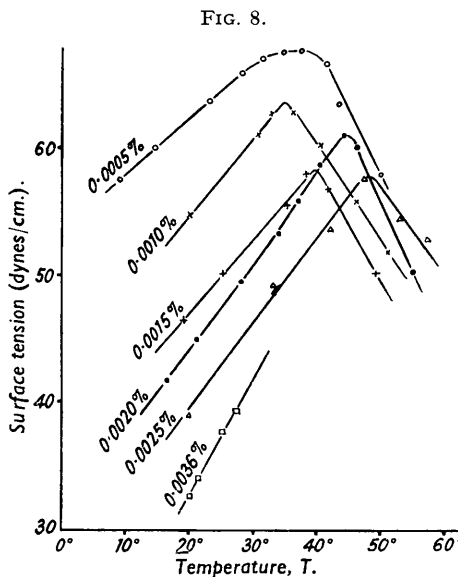


FIG. 8.

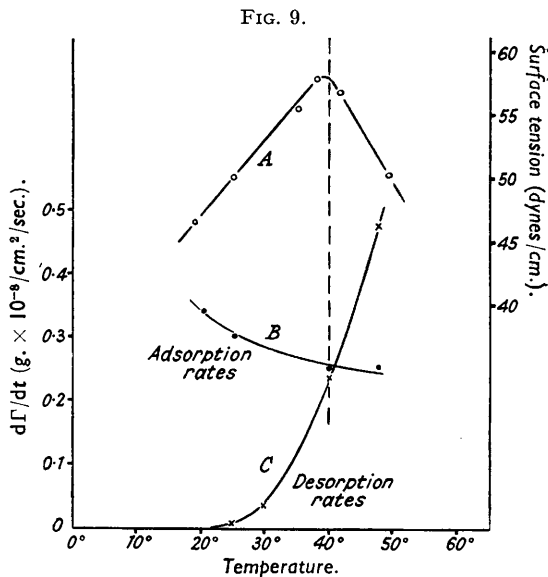


FIG. 9.

The two features (b) and (c) are probably closely related to one another, and may be considered together. Fig. 8 shows the relation between the equilibrium surface tension and temperature, over a range of concentration. This figure illustrates clearly the sharpness of the temperature inversion, and the constancy of the temperature coefficient on either side of the inversion point. The large positive temperature coefficient is probably to be attributed mainly to the differing sensitivity of adsorption and desorption rates to temperature. Since increase in temperature considerably increases the desorption rates but has no marked influence on the adsorption rates, the equilibrium surface excess will be appreciably reduced, with a consequent rise in the surface tension. The magnitude of the coefficient may also arise partly from the disorientation of the adsorbed molecules at the higher temperatures (Part XIV, succeeding paper). The adsorption and desorption rates, at any temperature, may be calculated from the data presented in this paper and Part XI (preceding paper). Fig. 9 shows calculated values (curves B and C) for a solution of concentration 0.0015%. The surface excess is considered as being displaced by equal amounts  $\pm \Delta\Gamma = 2.0 \times 10^{-8}$  g./cm.<sup>2</sup> from the equilibrium value at each temperature, and the rate at which the system moves to equilibrium is expressed as  $d\Gamma/dt$ . It will be seen from Fig. 9 that the inversion temperature (Curve A) is the temperature at which the rates of adsorption and desorption become equal. The position of curves B and C may be slightly incorrect owing to the use of the Gibbs equation in determining  $\Delta\Gamma$  at the higher temperatures, but this will not be sufficient to alter the general picture. Although it is clear from the above considerations that there should be a change in the direction of the  $\gamma$ - $T$  curves (Figs. 8 and 9) at the point where the two rates become equal, the rapid fall which occurs thereafter is not readily interpreted. Increase in surface pressure with increasing temperature is characteristic of insoluble films, but it seems unlikely that the film may be treated as insoluble over temperature ranges at which

desorption rates are highest, and further work is in progress in an attempt to elucidate this feature.

*Chain Length.*—In order to determine whether the compression of the surface film by pouring the solution is an effect which is peculiar to decyl alcohol, similar experiments have been carried out on solutions of shorter-chain alcohols, and the results are shown in Fig. 10. The effect persists down to  $C_7$ , but is scarcely detectable at  $C_6$ . As chain length decreases, the extent to which the films may be compressed also decreases, and the time required for re-establishment of surface equilibrium is reduced. The equilibrium values of tension recorded in Fig. 10 have no particular significance; concentrations were so chosen that each solution gave a similar initial tension.

There is an almost linear relationship between the extent of the upward drift  $\Delta\gamma$  under standard conditions, and the chain length. The results are consistent with the view that as chain length decreases the solubility in water increases, and there is a consequent fall in the value of the energy barrier to desorption (compare the corresponding increase in energy barrier to adsorption, Part XI, preceding paper). This view is supported by parallel experiments carried out on the corresponding straight-chain carboxylic acids and on *sec.*-octyl alcohol. For a particular chain length, the replacement of the  $\text{CH}_2\text{OH}$  group by the more hydrophilic  $\text{CO}_2\text{H}$  group results in an increased solubility and might be expected to reduce the compressibility of the film. This is found to be the case; the  $\Delta\gamma$  values for *n*-octoic and *n*-decoic acids are 1.5 and 5.7 dynes/cm., respectively, compared with 4.3 and 8.5 dynes/cm. for the corresponding alcohols. Again, the greater solubility of *sec.*-octyl alcohol compared with the straight-chain compound is reflected in the lower compressibility of the film ( $\Delta\gamma = 2.0$  dynes/cm.).

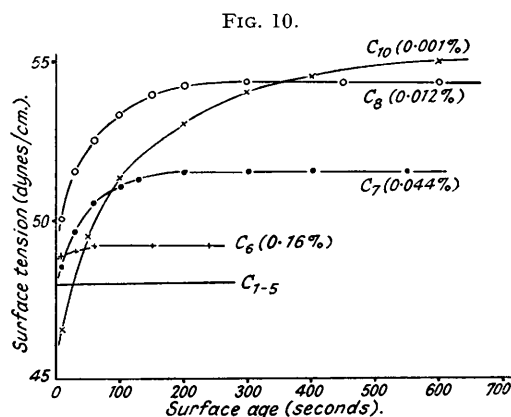
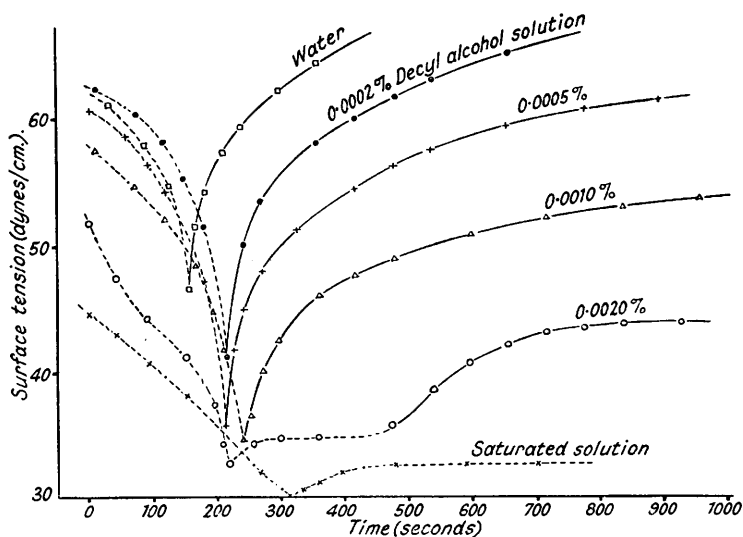
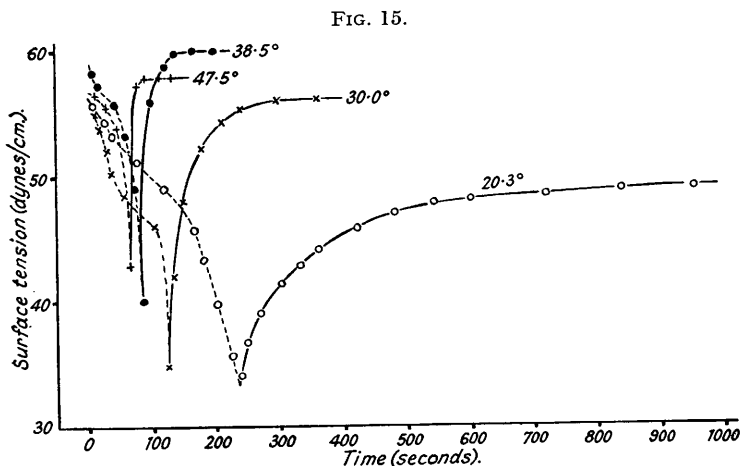
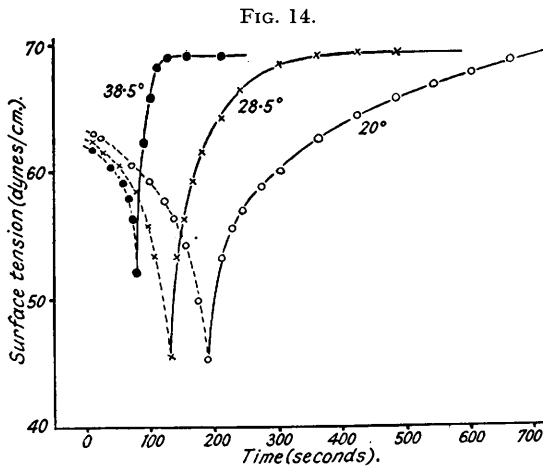
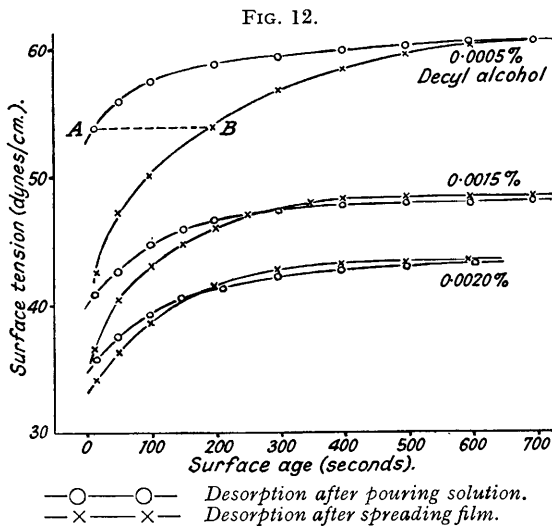
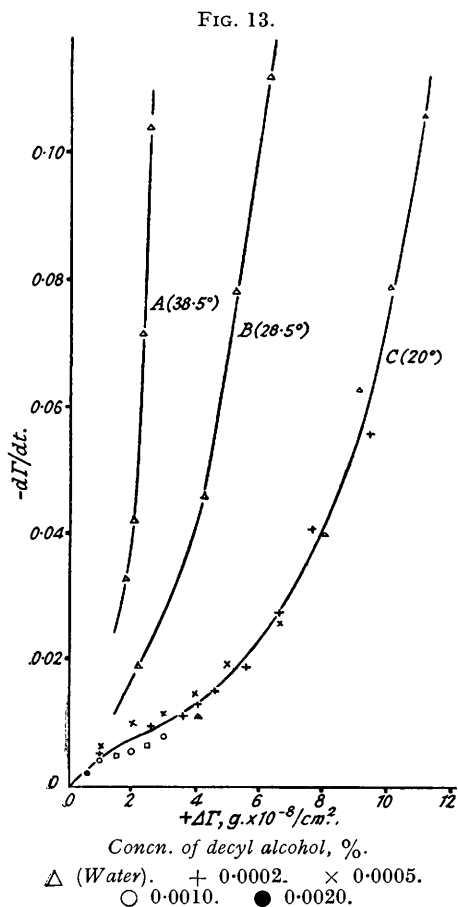


FIG. 11.



*The Spreading of Decyl Alcohol Films.*—Because of the desorption which occurs before measurement can be commenced, the desorption curves obtained by the "compression-by-pouring" technique represent only part of the available tension range, particularly with the more dilute solutions. Therefore, in order to obtain (a) direct confirmation that the results described above are, in fact, due to surface compression and subsequent desorption, and (b) desorption





curves extending over a wider surface tension range, films of decyl alcohol have been spread on the surface of water and decyl alcohol solutions and the changes in tension followed by means of the vertical plate. In each experiment the vertical plate was applied to the surface, which was then allowed to come to equilibrium. The film was applied by dropping on to the surface (at some distance from the plate) 0.1 ml. of a *n*-hexane solution. This quantity of hexane solution contained  $2.8 \times 10^{-6}$  g. of decyl alcohol, equivalent to a little more than three times the monolayer quantity. At concentrations below about 0.0015% the tension fell rapidly as the decyl alcohol spread from the lens and the hexane evaporated. This stage in the experiments has less significance in the study of the film, and the presence of a lens is represented in Fig. 11 by broken lines. (All measurements were carried out at 20°.) The lens gives rise to a spreading pressure on the surface film and since no tension has been observed in these experiments which is appreciably below the monolayer value, it follows that desorption from a compressed monolayer into a solution which is not saturated must be very rapid. At the moment when the lens disappears the spreading pressure vanishes and the tension immediately begins to rise. The subsequent true desorption curves are given in Fig. 11 by full lines. On the more concentrated solutions the lens is still present at the end of the initial tension fall; the tension then remains at about the monolayer value until the lens disappears. The lens does not, of course, disappear, and no increase in tension is observed, in the case of the saturated solution.

Confirmation that the tension changes obtained by the pouring technique are due to compression of the surface film is obtained by superimposing desorption curves obtained at 20° by the spreading and pouring techniques (Fig. 12). At 0.002% concentration the initial tension obtained by each technique corresponds approximately to a monolayer, and the two desorption curves are almost identical. In the more dilute solutions it is not possible, by the pouring technique, to approach the monolayer, and the apparent differences between the two curves arise merely from their differing positions on the time axis. For instance, if a monolayer formed by spreading decyl alcohol on a solution of 0.0005% concentration is allowed to desorb, the state of the surface after 200 seconds (*i.e.*, at *B*, Fig. 12) is the same as that initially formed by pouring the solution (*i.e.*, at *A*, Fig. 12).

*Factors influencing Desorption Rates.*—For any given solute three factors may influence rates of desorption from a surface film: (*a*) the bulk concentration of solute, (*b*) the amount of adsorbate in the film in excess of the equilibrium quantity, and (*c*) the temperature of the solution.

(*a*) and (*b*) *Influence of concentration.* It is clear from Fig. 11 that the rate of desorption varies considerably with the concentration of the solution. However, there are two separate properties which are determined by the concentration, *i.e.*, the equilibrium surface excess, and the number of molecules of solute in the liquid phase. The rates of desorption, recorded in Fig. 11, may depend upon both, or only one, of the above factors. In order to separate these two factors, rates of desorption (expressed as  $-d\Gamma/dt$ ) have been calculated from the results in Fig. 11, and are plotted in Fig. 13, curve *C*, against the amount of adsorbate  $\Delta\Gamma$  in excess of the equilibrium quantity. The results for all concentrations lie close to a single smooth curve. The  $\Delta\Gamma$  range over which  $-d\Gamma/dt$  may be measured becomes more restricted as concentration increases, but the results on curve *C* indicate that the bulk concentration has, in itself, little influence on the desorption rates when compared with the influence of surface excess.

(*c*) *Influence of temperature.* The pouring experiments indicated that change in temperature has a considerable influence on both desorption rates and the equilibrium tensions. The spreading technique has the additional advantage that it enables desorption curves to be obtained which are not modified by change in the equilibrium tension. Fig. 14 shows desorption curves obtained by spreading films of decyl alcohol on a water surface at different temperatures. Since the amount of decyl alcohol spread is insufficient to give rise to any appreciable bulk concentration, each curve returns to the water value for that temperature, and the profound effect of temperature changes on the desorption rates is in accord with that already observed (Figs. 5—7). Fig. 15 shows results obtained in parallel experiments employing a solution of 0.0014% concentration. The general form of the desorption curves is similar to that obtained for water (Fig. 14) but the temperature-inversion effect (Fig. 8) is now superimposed.

Desorption rates at 38.5° and 28.5° have been added to Fig. 13 (curves *A* and *B*, respectively) for comparison with the results at 20°. It is clear from this figure that desorption rates depend largely on temperature and surface excess, and that bulk concentration is of less importance.