708. *The Properties of Freshly Formed Surfaces. Part XI. Factors Influencing Surface Activity and Adsorption Rates in Aqueous Decyl Alcohol Solutions.*

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The solubility of decyl alcohol in water has been determined, and previous quantitative studies of the surface activity of aqueous solutions of straight-chain alcohols have now been extended to the decyl alcohol–water system. The paper gives a review of the main features of the system. The significance of surface tensions, as measured by the vertical-plate, pendant-drop, and expanding-drop methods, is discussed critically. Dynamic tensions have been measured over a range of concentration; the adsorption rates are found to be in satisfactory agreement with predicted values and from these rates the energy barrier to adsorption has been evaluated. An attempt is made to consider individually the various factors which determine the magnitude of this energy barrier.

EARLIER studies on aqueous solutions of the straight-chain alcohols (Part IV, *J.*, 1945, 98) suggested that an accurate study of the decyl alcohol system might be severely restricted by the low solubility of this alcohol (0·0036% at 20°, cf. 0·0050% for decoic acid). It has now been found possible to prepare standard and stable aqueous solutions of decyl alcohol, and the system has been found worthy of investigation for the following reasons.

(1) *Compressibility of surface film.* The surface tension of soluble films of C_1 to C_6 alcohols is not influenced by change in surface area. The effect is only slight at C_7 and C_8 but the surface tension of decyl alcohol solutions may be decreased by as much as 10 dynes/cm. by reduction in surface area. Since the molecule is simple, the compressibility of the film may be readily interpreted in molecular terms, and the system falls in that interesting region between the truly soluble and the truly insoluble films. In some cases where the compressibility of films of slightly soluble substances has been studied, *e.g.*, benzopurpurin solutions (Doss, *Proc. Ind. Acad. Sci.*, 1936, **4**, 11) and soap solutions (McBain and Wilson, *J. Amer. Chem. Soc.*, 1936, **58**, 380), the systems chosen have been less ideal in that the surface films may be influenced by micelle formation, change in pH, etc. These difficulties do not arise with decyl alcohol solutions. The compressibilities of phenol, β-phenylpropionic and octoic acids, studied by Ford and Wilson (*J. Physical Chem.*, 1938, **42**, 1051), occurred only at aged surfaces and are not directly comparable.

(2) *Rates of desorption.* When, as a result of surface compression, the surface contains an amount of adsorbate in excess of the equilibrium quantity, this excess is desorbed into the bulk solution. With the shorter-chain alcohols this desorption is very rapid and thus the films cannot be compressed. With decyl alcohol desorption is slower and may extend over several minutes; a quantitative study of the desorption process has been made.

(3) *Expansion of surface.* Expansion of soluble films of sodium dodecyl sulphate (Part IX, *J.*, 1948, 943) and decoic acid (Parts IV, *loc. cit.*, and VIII, *J.*, 1948, 936) has been shown to influence the surface activity of the adsorbed molecules. Decyl alcohol solutions show a similar effect, and tension measurements at expanding surfaces are of use in interpreting this effect, and also in assessing the relative significance of chain length and polar group.

(4) *Rates of adsorption.* The agreement found between the rates of adsorption determined by the vertical-plate method and the rates forecast by the empirical equation given in Part V (*J.*, 1945, 354) provides interesting confirmation of the vibrating-jet results, and indicates that as far as surface properties are concerned decyl alcohol takes its appropriate place in the homologous series.

(5) *Energy barrier.* As with the shorter-chain alcohols, the rates of adsorption in decyl alcohol solutions indicate the existence of an energy barrier. Its magnitude has been evaluated, and compared with known values for the shorter-chain alcohols.

(6) *Solubility of decyl alcohol.* The solubility of decyl alcohol in water is normally considered to be negligible, and even in studies on films at oil–water interfaces E. Hutchinson (*J. Colloid Sci.*, 1948, **3**, 219) takes no account of the solubility of this alcohol in the aqueous

phase. Even though the solubility is small, an accurate knowledge of its value is important in view of the high surface activity of decyl alcohol. Surface-tension measurement appears to be one of the few reliable methods available for determining the solubility.

In the present paper consideration is given to aspects (4), (5), and (6), above, and to the applicability of the vertical-plate, drop-weight, and pendant-drop techniques in the decyl alcohol system.

EXPERIMENTAL.

Purity of Decyl Alcohol.—The material used was "*n*-decyl alcohol" supplied by Messrs. Lights Ltd. It had b. p. 231°/749 mm. (uncorr.) (compare 232·9°/760 mm., Lecat, *Rec. Trav. chim.*, 1927, **46**, 245; and 228—232°, Schrauth, Schenck, and Stickdorn, *Ber.*, 1931, **64**, 1318), and m. p. 6·0° (compare 6·88°, Hoerr, Harwood, and Ralston, *J. Org. Chem.*, 1944, **9**, 267; and 6·4°, Verkade and Coops, *Rec. Trav. chim.*, 1927, **46**, 908). Although the alcohol appeared to be pure, the b. p. and m. p. alone were not taken as criteria of purity owing to the high surface activity of near homologues. Accordingly, the alcohol was vacuum-distilled, and the distillate collected in five separate fractions. No variation in distillation temperature was noted. B. p.s and m. p.s, refractive indices, and static tensions for a given concentration (measured by the vertical-plate method) were then measured for each fraction, and no variation in the values was found. Hence the alcohol was considered pure.

Preparation of Solutions.—The decyl alcohol (0·01—0·015 g.) was inserted into a weighed thin-walled glass capillary, open at both ends, by means of a very fine glass syringe, and the capillary tube and contents weighed. The capillary was submerged in the appropriate volume of distilled water (usually 1 l.) contained in a Pyrex-glass flask and was then broken by means of a glass rod. The alcohol was dissolved by continuous gentle swirling of the flask for 2—3 hours. This method was used to prepare solutions of concentration 0·001% and higher. More dilute solutions were obtained by dilution of the standards. No deterioration of the solution was found over a period of several days, provided that it was kept in a glass-stoppered vessel. In an unstoppered flask, appreciable loss of decyl alcohol occurred if the temperature was raised above 50°.

Methods of Surface-tension Measurement.

(*A*) *Stationary Surfaces.*—(1) *Vertical-plate method.* The apparatus used was essentially the same as that described in Part VII (*J.*, 1948, 930). A slight modification was made in that the arm of the balance was counterbalanced by a light aluminium vane. This had the effect of reducing the torque on the torsion wire and thus gave a linear γ-scale reading relationship over the whole tension range instead of the curve shown in Part VII (*loc. cit.*).

The choice of a suitable material for the plate depends upon the solution concerned. For instance, sodium dodecyl sulphate solutions give zero contact angle on a platinum plate, but give poor wetting on glass. In contrast, decyl alcohol solutions would not easily wet a platinum plate, there being a tendency for the wetted film on the plate to break up into drops almost immediately after its formation. However, when a glass plate was used (dimensions 5·0 × 2·58 × 0·0149 cm.) no such difficulty was encountered. The glass plate was suspended from the arm of the balance by means of a thin platinum wire; the wire was attached to the glass by adhesive wax and passed loosely through a hole in the arm. The glass plate was cleaned by immersion in concentrated nitric acid followed by several rinsings with distilled water. It was then dried by absorbent paper.

For the measurement of adsorption rates the decyl alcohol solutions were contained in a rectangular trough (inner dimensions 10 × 6·43 cm., and 10·5 cm. deep) which had a ground-glass edge coated with a smooth layer of paraffin wax. A wax-coated glass barrier was used to sweep the surface of the solutions. In determining an adsorption curve, the surface was rapidly swept (this required not more than 1 sec.) and a stop-watch was started simultaneously. The plate was lowered into the solution immediately, and the tip of the balance arm lightly tapped to give zero contact angle. As adsorption to the surface proceeded, the plate rose smoothly through a distance of up to 1 cm. Where necessary a correction was applied to allow for the length of wetted plate (Part VII, *loc. cit.*). In measurements of tension which involve no time factor it is convenient to control the movement of the plate relative to the surface (in order to maintain zero contact angle) by means of the movable pointer attached to the torsion wire. However, when the surface tension is changing within a short time interval, accurate control by this means is not possible. In this case the above method of initially tapping the arm lightly without altering the position of the pointer was found to be satisfactory.

Experiments were carried out in which changes in tension were followed at surfaces (*a*) in direct contact with air and in the absence of draughts, and (*b*) in an enclosed space which was allowed to come to vapour equilibrium with the liquid. The small amount of evaporation from the surface under conditions (*a*) appeared to make no appreciable difference to the surface properties of the solution, as recorded by the vertical plate. Therefore the vertical-plate surface-tension measurements recorded in this and following papers were carried out at surfaces shielded from all draughts but in direct contact with air, and hence represent solution–air rather than solution–saturated vapour values.

(2) *Drop-weight method.* This consisted essentially of expelling a drop of approximately known volume rapidly (within 1—2 sec.) from a calibrated orifice and measuring the time necessary for the tension to fall to such a value that the drop fell away. Since adsorption to the expanding drop surface is negligible during the initial 1—2 seconds of formation of the drop, adsorption can be considered as occurring at a stationary surface throughout. The details of the technique, as applied to decoic acid solutions, have been described in Part VI (*J.*, 1946, 579). However, in contrast to the vertical-plate trough measurements, evaporation from a drop surface had a profound effect on the measured tension values, and the results were quite unreproducible unless precautions were taken to avoid evaporation. Therefore, in these measurements the orifice (0·27 cm. outside diameter) was surrounded by a small glass vessel (approximately 10 ml. in volume and containing a little of the actual solution

under test) which was weighed before and after the fall of the drop. The closed space surrounding the orifice was allowed about 10 minutes in which to establish the necessary equilibrium vapour pressure before formation of the drop.

(3) *Pendant-drop method.* A single experiment by the drop-weight method gives only one point on the tension–surface age curve. This disadvantage is overcome if the surface tensions are obtained by calculation from the dimensions of a pendant drop. Andreas, Hauser, and Tucker (*J. Physical Chem.*, 1938, **42**, 1001) photographed the magnified image of a drop thrown on a screen and deduced the surface tension from the horizontal and vertical dimensions of the drop. We have found that a simple modification involving only drop-length gives accurate results.

A drop of the solution of known and predetermined volume (smaller than that equivalent to the lowest tensions to be reached) was rapidly formed on the same orifice as that used in the drop-weight measurements. The drop, which was illuminated directly from behind, was observed through a microscope carrying an eyepiece scale. A series of solutions of *iso*amyl alcohol of known surface tension were used for calibration. A drop of each solution (each drop identical in volume) was formed on the orifice, and the calibration curve relating drop-length with tension thus obtained. The drop of test solution was then formed on the orifice, and the whole time–tension curve obtained directly from the movement of the drop perimeter over the eyepiece scale. In order to avoid evaporation errors, the orifice was surrounded by a closed vessel having an optically plane glass side and containing a few ml. of the solution under test.

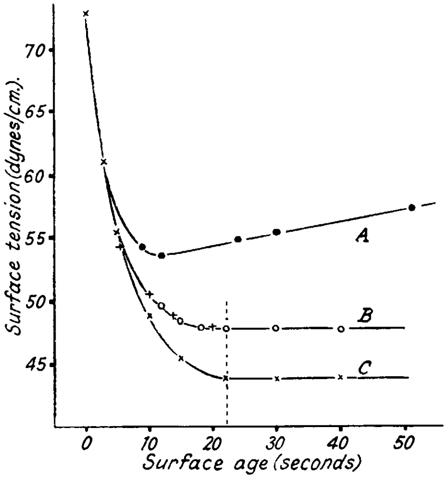
(*B*) *Expanding or Contracting Surfaces.*—(1) *Expanding-drop method.* The method used was the same as that described in Parts VI and IX (*locc. cit.*) and similar precautions were taken to avoid evaporation losses.

(2) *Trough method.* Expanding or contracting decyl alcohol films may be conveniently studied by varying the surface area of the solution, contained in a trough, by means of a movable barrier. Tension changes were recorded by the movement of the vertical plate. The results of this work are reported in Parts XIII and XIV (this vol., pp. 3404, 3406) and the experimental details are recorded therein.

DISCUSSION AND RESULTS.

True and Apparent Surface Tensions.—In contrast to most simple adsorbates, the surface-tension measurements recorded below (obtained by the drop-weight, pendant-drop, and vertical-plate methods) indicate that the values obtained, in the case of decyl alcohol solutions, are dependent upon the method of measurement. Fig. 1 shows the surface tension–time curves measured for a 0·002% solution by the three methods. Typical results obtained by the pendant-drop method in air are also given for comparison (curve *A*). The results obtained by the two drop methods are in close agreement when precautions are taken to avoid evaporation (curve *B*), but there is a marked difference between the adsorption curves obtained by the drop and the vertical-plate method (curves *B* and *C*). The discrepancy between the two curves is not apparent in the early stages of adsorption but increases as adsorption proceeds until at equilibrium the tension recorded by the latter method is 4 dynes/cm. lower than that by the drop method. Curve *A* indicates that evaporation from the drop surface results in an increase in surface tension and a consequent fall in the time taken to reach minimum tension. The high values given by the drop methods (curve *B*) as compared with the vertical-plate results cannot be attributed to evaporation effects since the time taken to establish equilibrium is identical with that recorded by the vertical plate. Again, the position of curve *B* was not altered by increasing the time during which the orifice was allowed to remain in the vapour cell before expulsion of the drop. A strict comparison between curves *B* and *C* should involve the solution–vapour results obtained by the vertical plate, instead of the solution–air tensions recorded in curve *C*. The magnitude of this difference is not of significance in these experiments, but it should be noted that the solution–vapour results would lie slightly below curve *C*.

FIG. 1.



0·002% *Decyl alcohol solution* (20°).

—●—●— *Pendant-drop method in air.*
—○—○— *Pendant-drop method in cell.*
—+—+— *Drop-weight method in cell.*
—×—×— *Vertical-plate method.*

Although the solutions used were extremely dilute, a simple calculation shows that the amount of decyl alcohol required for the formation of a film at the trough surface was insufficient to make any appreciable difference to the concentration of the solution. In view of the much larger area/volume ratio involved, the possibility that a drop of solution may become partly denuded of solute during the adsorption process could not be overlooked; but it may be calculated that a drop of 0·002% solution of size equivalent to a tension of 48 dynes/cm. contains $5{\cdot}6 \times 10^{-7}$ g. of decyl alcohol, whereas the formation of a close-packed monolayer on the surface of the same drop would require only $0{\cdot}5 \times 10^{-7}$ g. of alcohol. Any slight fall in concentration in the drop will be replenished by diffusion from the orifice tube so that the high pendant-drop tensions cannot be attributed to this cause. Again, in a drop pipette there is a large area of glass surface containing a small volume of liquid; if decoic acid solutions are allowed to stand in a drop pipette the concentration in the solution falls owing to adsorption of the acid at the glass surface with consequent increase in the measured tensions. However, similar experiments with decyl alcohol solutions have shown that adsorption at the glass surface does not occur.

TABLE I.

Concn. of decyl alcohol, %		0·0005	0·001	0·0015	0·0020	0·0025	0·0030
Surface tension, dynes/cm.	Vertical-plate method	62·5	54·8	48·4	43·5	39·5	36·0
	Pendant-drop method	62·9	56·9	52·5	48·4	44·9	41·6

Table I shows the surface-tension values determined for decyl alcohol solutions by the vertical-plate and the pendant-drop method over a range of concentration. The discrepancy diminishes as concentration decreases and becomes negligible at tensions above about 64 dynes/cm. Experiments on solutions of shorter-chain alcohols have shown that below C_8 no discrepancy occurs and that at C_8 the discrepancy is little more than the experimental error. Since the discrepancy becomes wider as the surface excess increases (Fig. 1 and Table II) it is most readily interpreted as arising from the lateral adhesion between the adsorbed molecules. The vertical-plate method is known to record true surface pressures for insoluble as well as soluble films (Harkins and Anderson, *J. Amer. Chem. Soc.*, 1937, **59**, 2189), so lateral adhesion does not influence surface tension or pressures measured by this method. In contrast, any lateral adhesion in an adsorbed film on the surface of a hanging drop will tend to create a " bag " round the drop, and will be equivalent to an additional upward force acting on the drop. The measured tension in such a system will then be an apparent value only and the difference between the equilibrium tensions shown by curves *B* and *C* (Fig. 1) is a measure of the magnitude of this " bag " effect. In surface films of more complex molecules this effect may become considerable; thus Dognon and Abribat (*Bull. Soc. Chim. biol.*, 1941, **23**, 62) have shown that the apparent surface tensions of serum solutions may be increased as the result of this " bag " effect to values higher than that for pure water. Since this effect is not restricted to films of complex molecules, the statement of Andreas, Hauser, and Tucker (*loc. cit.*) that the pendant-drop method " permits an accurate study of changes in surface composition with time " may only be true provided that accurate times, rather than accurate tensions, are required.

Results obtained with expanding-drop surfaces provide support for the view that lateral adhesion between the molecules is responsible for the discrepancies discussed above. Fig. 2 shows the variation in surface tension of various decyl alcohol solutions at 16° with rate of flow of liquid into the drop, *i.e.*, with rate of surface expansion. The tensions increase with flow rate, since the rates of surface expansion are in excess of the rates at which diffusion to the surface can occur. At an expanding surface there can be no appreciable lateral adhesion, since the adsorbed molecules are moving away from one another. Since the vertical plate also records true tensions it is to be anticipated that the vertical-plate results (Points *A*) rather than the pendant-drop results (Points *B*) will form limiting values of the expanding-drop tensions at zero expansion rate, and Fig. 2 indicates that this is the case.

Tension–Concentration Curve.—In view of the above considerations, the surface tensions recorded by the vertical plate are regarded as the true solution–air values, and the calculations and discussion given below and in following papers are based on these values. The molar concentrations of *n*-alcohols required to lower the surface tension of water to 55 dynes/cm. have been given in Part IV (*loc. cit.*). Although the values of C_{n-1}/C_n follow Traube's rule approximately, the actual ratios increase from 3·02 at C_2 to 3·39 at C_8, with a mean value of 3·23. The increase of C_{n-1}/C_n with chain length persists to C_{10}; at 55 dynes/cm. the molar concentration of decyl alcohol is $6{\cdot}33 \times 10^{-5}$, so that the mean of the C_9/C_{10} and C_8/C_9 ratios is 3·62.

TABLE II.

Concn., %	0·00037	0·00067	0 ·0010	0·0019	0·0024	0·0036
Γ, 10^{-8} g./cm.^{2}	4·3	6·8	8·8	11·5	12·0	12·2

The Gibbs equation has been applied to the vertical-plate tensions to determine the surface excess over the concentration range, and the results are given in Table II. A surface excess of $12 \cdot 2 \times 10^{-8}$ g./cm.^{2} is equivalent to a monolayer of vertically-orientated decyl alcohol molecules having cross-sectional area 21·3 A.^{2}. The cross-sectional area of straight-chain alcohol molecules is given as 21·6 A.^{2} (Adam, " Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd edn., 1941, p. 50). This supports the view generally held (*e.g.*, Alexander, *Trans. Faraday Soc.*, 1942, **38**, 54) that surface films on more concentrated solutions of this type approximate to monolayers.

FIG. 2.

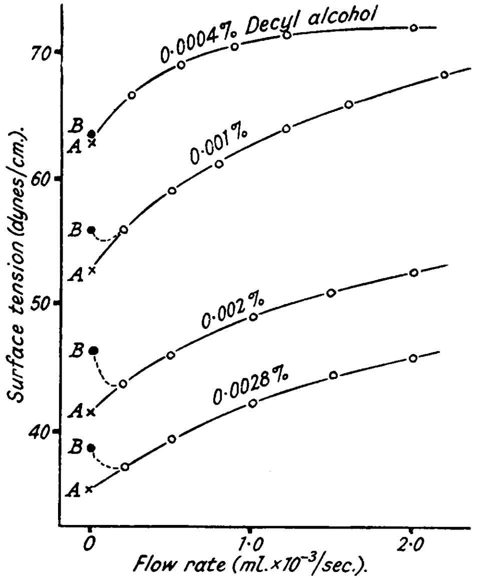
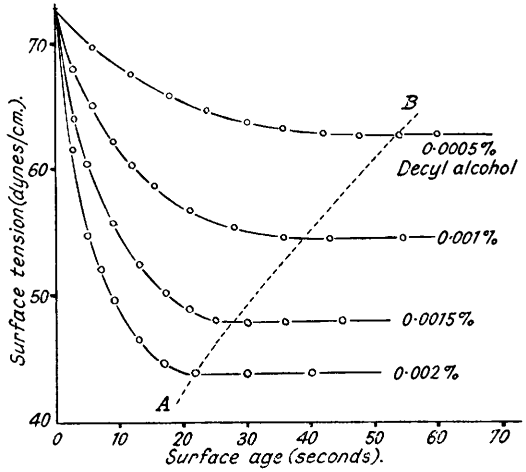


FIG. 3.



Rates of Adsorption.—The results obtained for decyl alcohol at 20° by means of the vertical-plate apparatus are recorded in Fig. 3. The broken line *AB* marks the boundary between dynamic and static surface tensions. The CO_2H group is slightly more hydrophilic than the $CH_2{\cdot}OH$ group and it is of interest to compare the times required to establish surface equilibrium in equimolar solutions of decyl alcohol and decoic acid. Some decyl alcohol values are compared, in Table III, with decoic acid values deduced from the measurements reported in Part VI (*loc. cit.*).

TABLE III.

Concn. (Molar × 10^{-5}).	Time to attain surface equilibrium (secs.).	
	Decyl alcohol.	Decoic acid.
3·16	53	>360
6·33	39	62
9·49	28	38
12·66	22	28

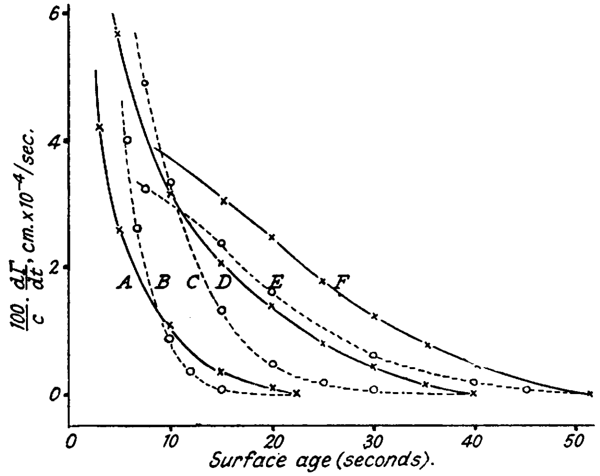
Adsorption curves for decyl alcohol solutions have also been obtained over the full concentration range by the pendant-drop method. As these are considered to be apparent values only, they are not reproduced here; at all concentrations they gave somewhat higher tension values, but the times required for establishment of surface equilibrium were in agreement with the vertical-plate values given in Fig. 3.

In Part V (*loc. cit.*) an empirical equation was deduced for the C_4—C_8 alcohols relating the rate of arrival of the molecules at the surface (*i.e.*, $d\Gamma/dt$) with time. This rate of arrival was expressed in terms of a " true " (rather than a mean) velocity v, where $v = (100/c)\, d\Gamma/dt$. Although v was employed as an empirical term, its use may lead to misunderstanding (see, *e.g.*, Blair, *J. Chem. Physics*, 1948, **16**, 113) if it is related too closely with considerations of adsorption mechanism. It is therefore proposed to discontinue its use, and the empirical equation then becomes

$$\frac{d\Gamma}{dt} = \frac{c}{100} \cdot a^{n}te^{-akt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By extrapolation to C_{10}, the constants n and k become 2·1 and 10, respectively. Since the decyl alcohol solutions used are very dilute, $a = 28c$, where c is the percentage bulk concentration. Employing equation (1), values of $(100/c)d\Gamma/dt$ for three concentrations of decyl alcohol at 20° have been calculated and are shown by broken curves in Fig. 4. The values obtained experimentally (deduced directly from the data given in Fig. 3) are superimposed in Fig. 4 as full lines. In view of the fact that (*a*) the constants used in equation (1) were extrapolated values and (*b*) the equation was developed on the basis of adsorption times not exceeding 0·1 sec., the agreement is good and indicates that there is no fundamental difference between the factors governing the rapid adsorption of the short-chain alcohols and those controlling the slower adsorption in systems of the decyl alcohol type.

FIG. 4.



Decyl alcohol concn., %.	*Experimental curve.*	*Curve calc. from eqn.* (1).
0·002	A	B
0·001	D	C
0·0005	F	E

Solubility of Decyl Alcohol in Water.—The surface tension of a saturated solution of decyl alcohol, measured by the vertical-plate method, has been found to be 32·5 dynes/cm. at 20° (spreading experiments reported in Part XII, following paper, indicate that this is the tension which is characteristic of the decyl alcohol monolayer). Extrapolation of the tension–concentration curve (obtained from Table II) to 32·5 dynes/cm. gave the solubility of decyl alcohol at 20° as 0·0036%. The same value was obtained by expanding-drop measurements. The solubilities of the C_5—C_8 alcohols are listed in Part IV (*loc. cit.*). The value for butyl alcohol for 20° is given as 7·90% (Seidell, " Solubilities," p. 265). A linear relationship exists between chain length l and the logarithm of the solubility at 20°, which may be expressed by the equation $l = 5{\cdot}65 - 1{\cdot}78 \log S$, where $S = \%$ solubility. By the application of this surface technique it may be possible to determine the solubility of slightly soluble compounds of even longer chain lengths which are normally considered to give purely insoluble films.

The Energy Barrier.—It is clear from the foregoing that : (1) the changes in surface tension recorded in Fig. 3 arise directly from the adsorption process, and (2) the times concerned are considerably in excess of those which would have been observed had the adsorption involved only normal diffusion to the surface. Consequently, some form of energy barrier to adsorption must exist. For experimental reasons, accurate surface-tension measurements on some of the shorter-chain alcohols (*e.g.*, amyl alcohol, Part II, *J.*, 1944, 252) are only available over the latter part of the time range. In view of the slower adsorption rates experienced with decyl alcohol, tension measurements may be carried out over almost the whole time range.

The results in Fig. 3 may therefore be suitably employed in a quantitative study of the energy barrier and of the factors which determine its magnitude.

Although adsorption is accepted as a hindered process, the actual nature of the energy barrier must depend upon the system concerned. Doss (*Kolloid Z.*, 1938, **84**, 138; 1939, **86**, 205) has suggested that, in electrolyte solutions, the energy barrier may be electrical in character. With non-electrolytes such as decyl alcohol, electrical factors can have little significance, but there seems to be no reason why the energy barrier should not be purely kinetic, only those solute molecules possessing kinetic energy in excess of the barrier value being capable of penetrating the surface. Alexander (*Trans. Faraday Soc.*, 1941, **37**, 15) considers that the well-known slow changes in tension which occur after the establishment of initial equilibrium may arise from the penetration of the surface by additional molecules, and this picture may apply to the initial adsorption process also. Blair (*loc. cit.*) has obtained the equation

$$\epsilon^{\lambda/\boldsymbol{k}T} = \frac{2n_0(FJ + L\boldsymbol{k}T)}{F} \cdot \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

where n_0 is the bulk concentration, D the diffusion coefficient derived by Ward and Tordai (*J. Chem. Physics*, 1946, **14**, 453), and J and L are constants for a given solute. From this equation the energy barrier λ may be calculated from measured values of surface pressure F and surface age t.

This equation being used, the energy barrier has been evaluated for *n*-decyl and *n*-octyl alcohols from the adsorption data given in Fig. 3 and Part IV (*loc. cit.*). The results recorded in Table IV were obtained by using values of t at which F was half-way to its maximum value. Diffusion coefficients D were obtained by extrapolation from the data given by Ward and Tordai (*loc. cit.*).

TABLE IV.

Alcohol.	Concn., %.	J, cm.^{2} × 10^{-16}.	L.	D, cm.^{2} × 10^{-6}/sec.	λ, cals./mol.
n-Octyl	0·020	12·9	0·728	5·94	378
n-Decyl	0·002	7·03	1·026	4·75	176

The energy barrier values are plotted against chain length in Fig. 5 (full curve *B*) together with the values calculated by Blair (*loc. cit.*) from the C_5—C_7 alcohol results reported in Part IV (*loc. cit.*).

The empirical equation discussed earlier, equation (1), contains constants n, k, and a, the significance of which has not yet been defined in terms of adsorption mechanism. Since the equation applies over the full C_4—C_{10} range, at least one of these constants must be related to the energy barrier. The values of k for the appropriate chain length, multiplied by a constant factor of 8·32, are also recorded in Fig. 5 (curve *A*). This curve follows the energy barrier curve closely, so that k is clearly a function of the energy barrier.

All the values of λ shown by curve *B* (Fig. 5) are calculated for surfaces at which adsorption is half complete. In order to determine whether the magnitude of the barrier varied with the amount of surface excess, λ values have been determined at various stages in the adsorption process. This may be done by evaluating λ along a single adsorption curve or by employing various adsorption curves. Blair's results (*loc. cit.*) indicate that for the C_5, C_6, and C_7 alcohols there is little variation in λ. A small variation was observed at C_8 and the variation at C_{10} is quite appreciable. The highest calculated values are shown by the broken curve *C* (Fig. 5) and the divergence between curves *B* and *C* illustrates the significance of the surface excess. Values of λ calculated for various concentrations are plotted against the surface excess Γ in Fig. 6. With increasing Γ the magnitude of the energy barrier passes through a minimum; thereafter it rises rapidly and approaches asymptotically the monolayer value of $\Gamma = 12{\cdot}2 \times 10^{-8}$ g./cm.^{2}.

In order to interpret the shape of the curve in Fig. 6 it is necessary to consider in more detail the factors involved in the operation of the energy barrier. In penetrating into the surface film, adsorbate molecules are considered as being influenced by the following factors: (1) they must overcome the attraction of the water molecules; (2) they will be mechanically hindered by the adsorbed molecules already in the film; and (3) there will be a force of attraction (which is responsible ultimately for lateral adhesion) between the adsorbing molecule and those already adsorbed.

Factor (1) is the major influence, since it determines the order of magnitude of the energy barrier. As chain length increases the attraction between water molecules and solute molecules diminishes; this is apparent from the decrease in solubility and increase in surface activity, and on these grounds it seems reasonable that the energy barrier should also diminish with increasing chain length (Fig. 5). For the same reasons the reverse holds for the desorption process, and the energy barrier to desorption increases with increasing chain length (Part XII, following paper). Factor (1) may be considered to be independent of the state of the surface, but factors (2) and (3) are directly dependent on the surface excess. When the surface excess is small, an adsorbing molecule is unlikely to encounter any appreciable hindrance in penetrating the surface film. As the adsorbed molecules become more close-packed the difficulty of penetration will increase sharply. The significance to be attached to the orientation of solute molecules arriving at the surface will also depend on the surface excess. At small Γ values orientation is not likely to be important, but as the monolayer is approached, penetration of the surface may be restricted to those solute molecules which, on arrival at the surface, are orientated in the same direction as the adsorbed molecules. Factor (3) is unlikely to modify the energy barrier to more than a small extent. Whereas the operation of factor (2) increases the apparent energy barrier, factor (3) should decrease it to an extent approximately proportional to the surface excess. Factors (2) and (3) will operate together to modify the magnitude of the barrier as determined by factor (1). The mean effects of factors (2) and (3) should cause the curve to pass through a minimum of the type shown in Fig. 6.

Fig. 5.

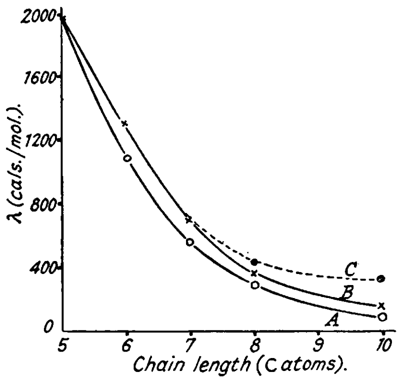


Fig. 6.

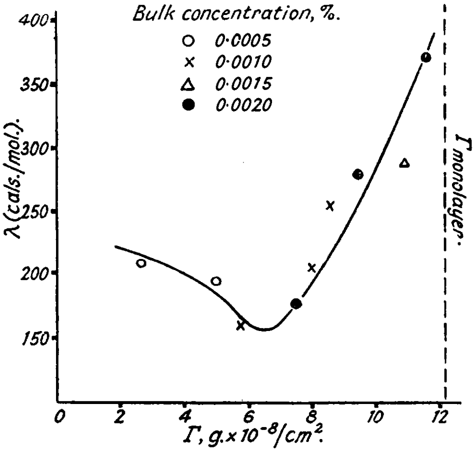
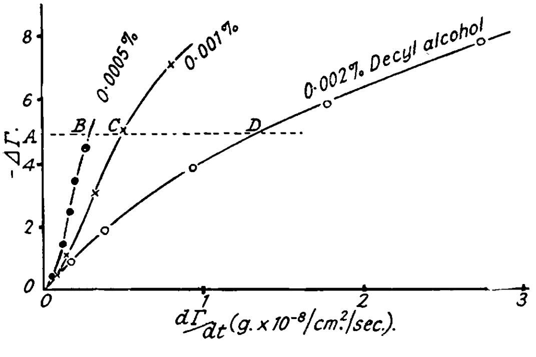


Fig. 7.



Further direct support for the existence of a minimum in the energy barrier curve may be obtained from a study of the rates of adsorption reported in Fig. 3. For a solution of any given bulk concentration there is a particular value of surface excess, which is equivalent to the lowest energy state for a surface of that solution. The rate at which solute molecules possessing the necessary kinetic energy will pass into the surface film depends, for a constant energy barrier and bulk concentration, on the extent to which the surface excess falls below the equilibrium value. If, then, we imagine the energy barrier to be constant, and consider solutions of various concentrations having the same surface deficit, the rate of arrival of molecules at the surface should be directly proportional to the concentrations of the solutions (assuming that the distribution of energy between the solute molecules in the bulk solution is not influenced in these dilute solutions by change of concentration). In Fig. 7 the rate of arrival of molecules at the surface ($d\Gamma/dt$) is plotted against the surface deficit $-\Delta\Gamma$ for three concentrations. For any given $-\Delta\Gamma$ value (*e.g.*, line *AD*, Fig. 7) the existence of a constant energy barrier would imply that $AD = 2AC = 4AB$. The measured ratios are listed in Table V.

TABLE V.

$-\Delta\Gamma$, g. × 10^{-8}/cm.^{2}.	Rate of arrival $d\Gamma/dt$. (1). $c = 0{\cdot}002\%$; $\Gamma_{\text{equil.}} = 11{\cdot}85$.	 (2). $c = 0{\cdot}001\%$; $\Gamma_{\text{equil.}} = 9{\cdot}05$.	 (3). $c = 0{\cdot}0005\%$; $\Gamma_{\text{equil.}} = 5{\cdot}45$.	Ratio (1)/(2).	Ratio (2)/(3).
1	0·21	0·15	0·10	1·40	1·50
2	0·42	0·24	0·15	1·75	1·60
3	0·68	0·33	0·19	2·06	1·74
4	0·98	0·41	0·24	2·39	1·71
5	1·35	0·51	0·30	2·64	1·70
6	1·80	0·62	—	2·90	—

The fact that the ratios shown in Table V deviate from a constant value of 2 implies that the energy barrier varies with surface excess, and an energy barrier curve of the general form shown in Fig. 6 is necessary to restore these ratios to 2. For example, for $c = 0{\cdot}002\%$ and $-\Delta\Gamma = 1$, $\lambda = 330$ cals./mol. (Fig. 6) and for $c = 0{\cdot}001\%$, $\lambda = 190$ cals./mol. This difference in λ may be regarded as responsible for the fall in ratio (1)/(2) to 1·40. Similarly, for $-\Delta\Gamma = 6$ and $c = 0{\cdot}002\%$, $\lambda = 160$ cals./mol. and for $c = 0{\cdot}001\%$, $\lambda = 210$ cals./mol., and since the ratios lie on either side of 2, it follows that the energy barrier curve must possess a minimum. The exact position of the curve in Fig. 6 cannot at present be drawn with sufficient accuracy to permit a fully quantitative study of these rates of adsorption, particularly at the smaller Γ values, but the above interpretation presents a clear picture of the significance of the energy barrier in the decyl alcohol system.

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