22. *The Variation of the Solubility of Unimolecular Films with Surface Pressure, and its Effect on the Measurement of True Surface Pressure.*

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Measurements of the surface pressure developed in films in presence of excess of the film-forming substance, made with a Harkins–Anderson surface balance, showed that, contrary to the belief of previous workers, this pressure is not constant. Investigation of its variation with time for cetyl alcohol on water at p_H 7·0 disclosed curious changes which are attributed to the combined effect of progressive solution of the film and varying immersion of the floating islands of excess alcohol. After the film has been swept off completely, bubbling of air through the water brings a film of cetyl alcohol to the surface, proving that solution has occurred. With octadecyl alcohol the pressure rises to a maximum and then falls progressively. This effect is not observed if the water is previously saturated with the alcohol.

Stearic and palmitic acids are similarly soluble, the latter very rapidly, in water at p_H 7·0, but much less soluble in N/100-hydrochloric acid. The solubility of a mixed film of stearic acid and cetyl alcohol (1 : 5) is less than that of either substance alone. Soluble films were also given by cholesterol, by proteins, and by oleic, elaidic, brassidic, and erucic acids. The solubility of arachidic acid was slight, and that of *n*-docosanol barely detectable.

It is suggested that unimolecular films in general may be regarded as saturated solutions of water in the film-forming substance in pseudo-equilibrium with underlying solutions of that substance in water which progressively decrease in concentration with depth.

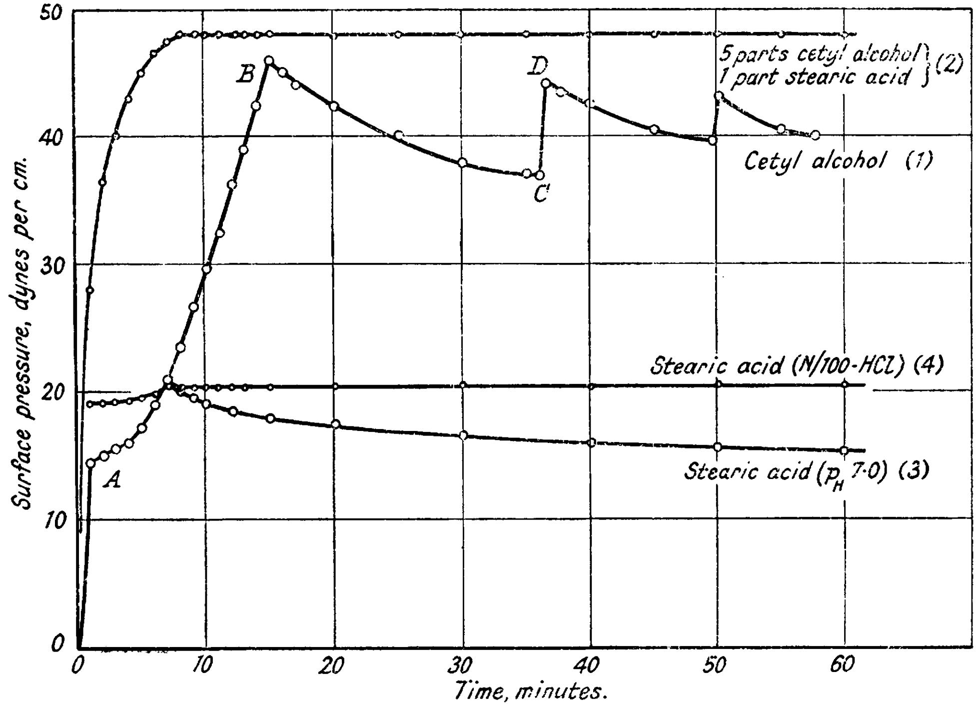
In the course of experiments on the effect of unimolecular surface films in reducing the rate of evaporation from the water substrate, it became necessary to measure the surface pressure exerted by a film in equilibrium with excess of the solid film-forming substance. Cary and Rideal (*Proc. Roy. Soc.*, 1925, *A*, **109**, 301), who studied the spreading of long-chain solids, found that at a given temperature the surface pressure of such a film had a definite value F_e. Our preliminary experiments, however, raised some doubt as to the constancy of this pressure, and so a more detailed study of the matter was undertaken.

The trough used, and the surface balance which was of the Harkins–Anderson type, have been fully described in the preceding paper. The substrate was distilled water, buffered to p_H 7·0 with sodium bicarbonate, and kept at a constant temperature of 19·5°. The benzene was purified as described in the preceding paper.

To facilitate the rapid attainment of equilibrium, the solid surface-active substance was dissolved in benzene, and small drops of the solution were placed on the clean water surface from a micro-pipette. The drops immediately spread to form a unimolecular sheet, the benzene evaporating. When the surface was completely covered with film, the excess solution remained, either as one small lens, or as a number of smaller lenses which tended to coalesce whenever they approached one another; after a few minutes the benzene evaporated, leaving little islands of the surface-active material, and it was assumed that under these conditions the constant pressure F_e (see above) would be observed. It was found, however, that the final pressure varied considerably within a certain range, and appeared to depend on the total quantity of solid on the surface. It seemed likely, then, that the pressure was not a true equilibrium pressure, and for that reason its change with time was investigated.

In every case, exactly the same quantity of benzene solution was placed on the water surface, and the surface pressure taken at one-minute intervals. When pressure was plotted against time, cetyl (hexadecyl) alcohol gave curve 1 in Fig. 1. The pressure *A* was reached immediately an excess of the benzene solution was placed on the surface and corresponds to the pseudo-equilibrium between a benzene solution of given concentration and a unimolecular layer of cetyl alcohol on the water. From *A* to *B* the benzene was evaporating, and hence with increasing concentration in the solution the cetyl alcohol exerted an increasing pressure. At *B* it is presumed that all the benzene had evaporated, leaving pure cetyl alcohol. The alcohol left floating on the surface as a large drop was usually liquid although its m. p. (49·5°) is much above the temperature of experiment (19·5°); this is probably due to the retention of small traces of benzene which do not easily evaporate, and this phenomenon is believed to be responsible for the curious curve obtained for cetyl alcohol, which is unlike those given by the other substances.

FIG. 1.



The drop in pressure from *B* to *C* is the most interesting feature: it is due to solution of the cetyl alcohol in the water. As the balance used employed no floating barriers, the possibility of leakage was eliminated, and three other possible explanations of the fall in pressure remain. (1) The effect of the benzene was to increase the spreading force of the cetyl alcohol, and when it had evaporated the pressure fell to the value representing the true spreading force of cetyl alcohol; (2) the alcohol was evaporating into the atmosphere; or (3) it was dissolving in the water. The first possibility seems inconsistent with the curious repetitive nature of the curve. As to the second possibility, it seems very improbable that a heavy molecule of such high b. p. should be readily volatile even when in a unimolecular layer, as it is presumably anchored by the hydrophilic hydroxyl group; Hardy (*Proc. Roy. Soc.*, 1913, *A*, **88**, 315) stated that ethyl cinnamate, a substance of quite high b. p., evaporates very rapidly when spread on water, but in view of the results here reported, it may well be that this observation is to be attributed rather to the solubility of the film.

That the drop in pressure is in fact due to the solubility of the cetyl alcohol is proved by the following experiment. A film of cetyl alcohol was left in equilibrium with excess bulk cetyl alcohol for some hours, and then the surface was thoroughly cleaned by passing barriers over it. The trough was covered, and left overnight. Next morning the cleaned balance slide was immersed in the liquid, and the barriers placed in position at either end of the trough. On reduction of the area between them, the motion of the balance soon showed that there was a film on the surface. A blank experiment gave no such film, and thus eliminated the possibility that there might be accidental contamination, or migration of surface-active material from the sides of the trough.

It is understandable that, although the dissolution from the film may be comparatively rapid, yet once the substance is in solution, the rate of its return to the surface may well be much less, being dependent on diffusion and convection. In order to hasten this process clean air was bubbled through the water. The cetyl alcohol which had been spread on the surface was first cleaned off by barriers, and it was then found that after air had been bubbled through for ten minutes, sufficient cetyl alcohol was brought up by the bubbles to show that some had certainly been held in solution. It seems that there must be an equilibrium between the amounts of cetyl alcohol in the surface and in the solution. The effect of blowing in air is to produce large surfaces in the body of the liquid, so that the chances of the dissolved cetyl alcohol becoming adsorbed on a surface are increased. These surfaces then rise to the true water surface where the cetyl alcohol remains until its surface concentration is high enough to send some back again into the bulk of the liquid.

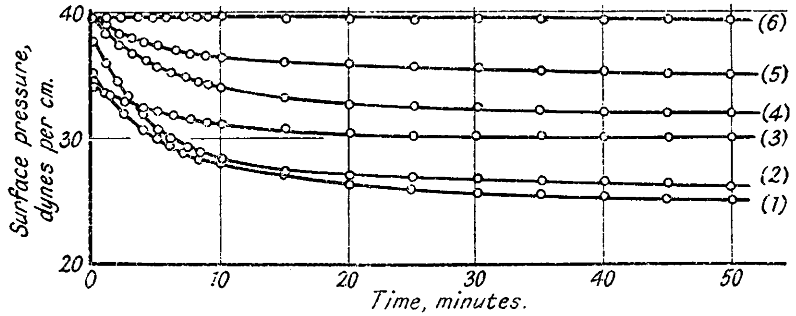
The curious rise in pressure, *CD*, which is very rapid, was difficult to understand until the behaviour of the lens of cetyl alcohol was carefully observed. When the pressure *B* is reached, this lens is pushed so far below the surface that the spreading from it is at a minimum, and with no substance to replace that going into solution, the pressure fell along *BC*. The explanation of this depends upon the fact that a body afloat on water is subject to the upthrust of the water on the part immersed, and to the surface tension acting along its perimeter. If there is an obtuse contact angle, as is the case when the substance is not wettable, any decrease of surface tension is equivalent to a force acting on the body in a direction opposite to the upthrust. In the case of cetyl alcohol, when the pressure *B* is reached, the surface force acting on the lens is sufficient to overcome the upthrust of the water and the lens is further immersed. At *C*, however, the lens broke through to the surface, and the cetyl alcohol rapidly spread again to give the new pressure *D*, which is slightly less than *B* owing to the smaller size of the lens. This affects the pressure in two ways: (1) If the film is constantly going into solution, the pressure is always a balance between the rate of spread from the lens and the rate of solution; and as the rate of spreading from the lens is proportional ***inter alia*** to the perimeter, the smaller lens produces a smaller surface pressure. (2) A smaller lens means a smaller upthrust; hence a smaller surface pressure will force it under the surface of the liquid.

This fluctuation will presumably continue until the lens has completely spread to a unimolecular film. The considerable difference between *B* and *C* is difficult to explain, but it may be due to the difference between a receding and an advancing contact angle. If the lens is disturbed by a platinum wire before the minimum is reached it immediately comes to the surface and spreads.

Octadecyl alcohol [Fig. 2 (1)] does not behave in quite the same way. Being an alcohol with a longer chain than cetyl alcohol, it exerts a lower maximum pressure, and this is not big enough to push the lens under the surface; for that reason there is simply one maximum. There is the usual rise in pressure as the benzene evaporates, and after the maximum is attained, the pressure falls at a decreasing rate until it becomes almost constant. This corresponds to the point at which the octadecyl alcohol is dissolving as rapidly as it spreads from the bulk phase. It is noteworthy that if some benzene is now added to the bulk octadecyl alcohol, the pressure falls to the equilibrium value for the benzene solution, rising again as the benzene evaporates to almost the same maximum pressure, and falling yet again, more slowly, to a pressure higher than that previously observed. Repetition of this process raises the final pressure still more [Fig. 2, curves (1)—(5)]. On sweeping the surface clean, and starting with a fresh quantity of alcohol, the whole sequence of curves could be repeated again. Repeated applications of benzene resulted in a film which only dissolved very slightly [Fig. 2, (5)] but it was not possible to obtain a film which did not dissolve at all. It would appear that if the water is not disturbed, a concentration gradient for the alcohol is developed ranging from a saturated solution at the surface to a very dilute one lower down. The final pressure observed is an arbitrary resultant dependent, *inter alia*, on the rate of spreading, the rate of solution, and the rate of diffusion of the dissolved alcohol away from the surface. Sweeping the surface clean disturbs the water, and assists in equalising the concentration of dissolved alcohol throughout the water.

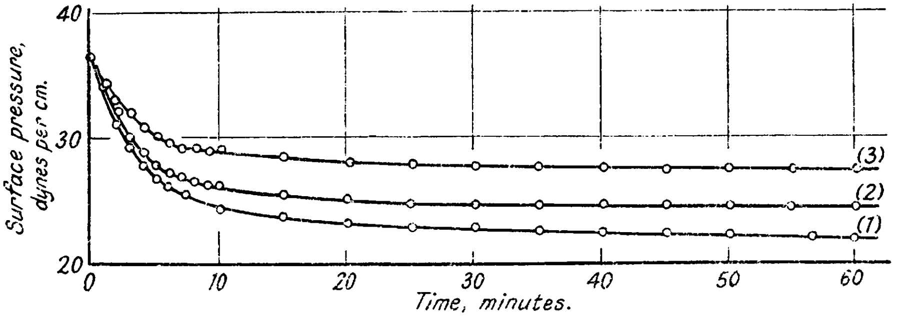
It would seem that the film on the surface is not a sharply defined unimolecular layer, but rather, a less definite layer of pure surface-active substance in which a small quantity of water is dissolved; from this there is a gradual transition to pure water in which a small quantity of surface-active material is dissolved.

Fig. 2.



The fact that the film is dissolving even in the region in the above curves when the pressure remained constant, was shown by spreading a unimolecular film of octadecyl alcohol on water without any excess, and compressing it between barriers to the maximum pressure previously noted. The pressure fell rapidly at first [Fig. 3, (1)], and later more slowly at a constant rate. On recompressing the film again to the same pressure, the pressure fell as in curve (2), and on a further repetition of the process as in curve (3). This agrees well with the previous observations.

Fig. 3.



The final proof that the phenomenon is due to solution was obtained by spreading a film on a saturated solution of octadecyl alcohol, prepared by adding a solution of this alcohol in 1 c.c. of absolute ethyl alcohol to 2 l. of water. The octadecyl alcohol was precipitated in a very finely divided form, and the solution was shaken for one hour. A film spread on this solution showed no drop in the final pressure over a long period [Fig. 2, (6)].

It must be emphasised that the quantities dissolved are always very small. With incompressible condensed films such as are here used, a small quantity of substance would make an appreciable difference to the surface pressure, but it was not considered that the slope of the normal force–area curves in this region was sufficiently accurately established to justify any calculations. Since, however, a fraction of a mg. of solid was sufficient to cover the surface of the liquid with a unimolecular film, and there was 1 l. of water as the substrate in the trough, it follows that the solubility is infinitesimal.

Fatty acids showed a similar solubility at p_H 7·0. Palmitic acid dissolved so rapidly as to preclude any accurate work on its effect on evaporation, for which a surface pressure constant for 10 minutes was necessary. Similarly, stearic acid at p_H 7·0 is soluble. On N/100-hydrochloric acid, however, it is apparently insoluble [Fig. 1, curves (3) and (4)]. Cary and Rideal (*loc. cit.*) recognised this solubility, for they worked on acid solutions in order to prevent what they called " soap formation."

Though both cetyl alcohol and stearic acid give soluble films on water of p_H 7·0, a mixture of them in the ratio 5 : 1 gives a curve of different characteristics if spread from excess solid [Fig. 1, (2)]. If the mixture is compressed between barriers to give the maximum pressure reached, the pressure very gradually falls, though not so rapidly as with either of the single substances. The maximum reached in the presence of excess solid is almost exactly that obtained as the maximum for cetyl alcohol alone. The effect of the added stearic acid, then, is to increase the rapidity of spreading from the solid, as well as to reduce the rate of solution from the film. The island in this case was solid, not liquid, so it was not forced under the surface of the water. This may account for the constancy of the pressure reading. This effect of mixing films offers an explanation of some curious phenomena. It had been noticed that mixed films of stearic acid and cetyl alcohol gave higher pressure readings than either of the pure substances. It is now obvious that the pressure readings obtained for the pure substances were really low owing to solubility, and that the addition of a second substance has the effect either of reducing the solubility of the first or of so disturbing the crystal forces as to increase the rate at which the film spreads from the solid, thus more readily compensating for the effect of solution.

In the course of the experiments it was observed that soluble films are given by cholesterol, proteins, and oleic, elaidic, brassidic, and erucic acids. For arachidic acid the solubility was slight, and for *n*-docosanol it was barely detectable.

As already indicated, the results suggest that in some cases it may be more profitable to consider a unimolecular film, not as a simple film of the substance spread, but as a solution of water in that substance in equilibrium with underlying solutions of the film-forming substance in water. The relationship between the concentration in the surface and that in the bulk, derived from the Gibbs adsorption equation, is $\Gamma = \frac{1}{RT} \cdot \frac{dF}{d \ln c}$, and it follows that an increase of F must increase the concentration in the bulk of the liquid. Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385) for the soluble fatty acids, and Schofield and Rideal (*Proc. Roy. Soc.*, 1925, *A*, **109**, 57; 1926, *A*, **110**, 167) for those from C_6 to C_{12} have shown that the Gibbs equation can be applied. Addink (*J. Chem. Physics*, 1934, **2**, 574) has recorded observations of force–area and surface potential curves for myristic acid showing slow changes with time, which could be followed for several hours by the change in phase-boundary potential and were attributed in part to the effect of solution. He inferred, as we do, that the film contains water and that the water content is reduced by increase of surface pressure.

The cases here dealt with are limiting cases where the concentration in the aqueous solution is very low, and in the case of docosanol the solubility is so low that the concentration in the water may be considered as zero.

There is thus a complete sequence from the very soluble short-chain compounds whose concentration in the surface phase is low, though detectable, through the appreciably soluble ones up to about C_{12}, then through those from C_{12} to about C_{18} where the bulk of the substance is in the surface but with a slight concentration in the water phase, to the completely insoluble compounds with over 20 carbon atoms in the chain, where the concentration in the water is negligibly small.

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