21. *The Evaporation of Water through Unimolecular Films.*

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A new technique has been developed for comparative measurements of the rate of evaporation of water through unimolecular films into a constant current of dry air under conditions of controlled and measured surface pressure. The device used is named the " evaporant," and its construction and use are described.

It is found that the resistance offered by films to the evaporation of underlying water is a highly specific property: some films, *e.g.*, of egg albumin, cholesterol, oleic acid and elaidic acid, offer practically no resistance under any conditions, whereas stearic acid, brassidic acid, arachidic acid, cetyl alcohol, octadecyl alcohol, and *n*-docosanol under suitable conditions can reduce evaporation to a very small fraction of that from a free water surface.

The resistance becomes substantial only above a critical surface pressure which is characteristic for each substance and is, in general, substantially greater than that at which the film becomes relatively incompressible. Hydrophilic groups in the chain appear to reduce or eliminate the resistance. Increase of chain length increases resistance and lowers the critical pressure at which substantial resistance sets in. The resistance of a film cannot be correlated with its physical state; *e.g.*, the solid film of albumin offers no resistance, but the liquid film of cetyl alcohol offers great resistance to the passage of water.

It is suggested that an explanation of these phenomena may require the assumption that unimolecular films contain dissolved water and are in equilibrium with a solution of the film-forming substance in the water substrate. Films of " indicator oil," even 100 molecules thick, offer less resistance to evaporation than typical " waterproof " unimolecular films such as that of cetyl alcohol.

But little is known about the effect of unimolecular films on the rate of evaporation from a water surface. Hedestrand (*J. Physical Chem.*, 1924, **28**, 1244) passed a rapid stream of dry air over a water surface on which he had spread palmitic or oleic acid, and by comparing the quantities of water taken up by the air with and without the presence of the film he concluded that such films do not affect the rate of evaporation. Rideal (*ibid.*, 1925, **29**, 1585) showed that Hedestrand's technique would not suffice to show any effect that these films might have had and, by distilling water in a vacuum from one leg of an inverted U-tube at 25° or 35° to the other held at 0°, he found that films of stearic, lauric, and oleic acids all had a marked effect on the rate of evaporation, giving at 25° reductions in that rate of 28%, 42%, and 52% respectively. In these experiments, Rideal spread his films on the water surface by adding a crystal or lens of the fatty acid to the surface and allowing it to remain for some hours until equilibrium between the bulk and a unimolecular film had been attained. It follows, then, that Rideal's figures show the effect on evaporation at surface pressures which are arbitrarily fixed for each substance and bear no significant relation to each other.

Langmuir and Langmuir (*ibid.*, 1927, **31**, 1719) discussed the results of previous authors and investigated the effect of unimolecular films on the rate of evaporation of ether from an ether–water mixture. They also examined the effect of certain films on the rate of evaporation of water into air by weighing water in petri dishes, at definite intervals of time, after placing films on the surface. They found no appreciable effect with oleic acid, myricyl alcohol, stearic acid, or cetyl palmitate, but noticed a decided diminution in evaporation with a film of cetyl alcohol. Similar work has subsequently been reported by Glazov (*J. Physical Chem. U.S.S.R.*, 1938, **11**, 484). Using Rideal's figures and considering separately the various resistances to evaporation from a liquid surface, Langmuir and Langmuir calculated a value R, the reciprocal of the rate of evaporation, which they called the resistance to evaporation. Rideal's results gave a value for R of 800 units for oleic acid and 300 units for stearic acid. For cetyl alcohol, they found R to be 65,000 units, a disproportionately high value for which they could give no explanation. These authors, too, worked under the natural limitations imposed by using each substance at its equilibrium pressure between the bulk phase and the unimolecular film.

It is evident that the experimental methods employed in these earlier investigations were such that it was impossible to change and control the surface pressure of the unimolecular film investigated, and it was felt it would be useful to study the evaporation of water through films spread on a Langmuir–Adam trough under accurately known and controlled conditions. The results of this investigation have shown that the surface pressure of the film greatly influences its effect on evaporation. If surface pressure is taken into account, the apparent anomalies of the earlier results are explained, and certain new and interesting phenomena are observed.

For the present purpose it seemed that more useful results would be obtained if, instead of concentrating on absolute rates of evaporation, comparative results were sought by using different films in varying states of compression, but under conditions which for a pure water surface would always give the same results. The original objective was to get some indication of the effect of films upon evaporation from large surfaces into air at atmospheric pressure, with a view to their possible practical application to minimise the evaporation of stored water in dry climates. Therefore a comparison was made of the effects of films on the rate of evaporation into dry air. An obvious advantage of this method as against the measurement of the rate of evaporation into a vacuum is that evaporation into air is much slower and therefore more easily controlled, though against it is the fact that the effect of a film on evaporation into a vacuum would probably be much more marked, and might disclose differences which the slower method would obscure.

The principle of the method adopted was to pass a constant stream of dry air over a known area of the water surface with and without a film, and to collect and weigh the water evaporated into that air in a fixed time. As the rate of evaporation of water at room temperature, even into an air current, is very rapid, and as, obviously, useful comparative data could be secured only if it were certain that at no stage of its passage over the water surface was the air saturated with water vapour, the rate of air flow had to be fairly high and the path length small.

EXPERIMENTAL.

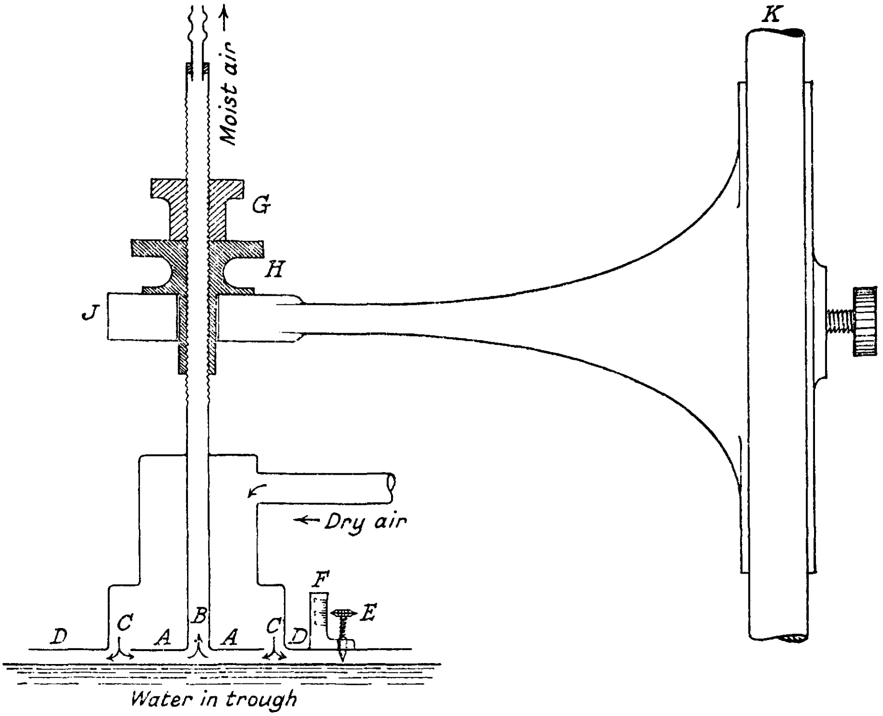
With these conditions in mind, the apparatus shown in Fig. 1 was designed, which for convenience may be named the " evaporant."

The essential feature is a brass disc, A, carried by a central brass tube B, the axis of which is precisely perpendicular to the disc. This disc is set parallel to the film under investigation, at an exactly determined distance from the surface, and a stream of dry air is drawn radially inwards between the disc and the surface and up through *B*, whence it passes to the absorption apparatus where the evaporated water is collected for weighing.

It is essential that the air drawn shall be initially perfectly dry, and to ensure this a current of dry air is fed to the periphery of the disc *A* through the annular space *C* at about twice the rate of withdrawal, the excess passing away below the outer disc *D* and so excluding the outer air.

The outer disc *D* is made accurately co-planar with *A* and is provided with a pointed adjusted screw, *E*, the setting of which can be read on the scale *F*. The evaporant as a whole is suspended from an adjustable flange *G* screwed upon the upper part of the tube *B* : *G* is accurately plane on the underside and rests upon the plane upper surface of the boss *H*, which can rotate smoothly and freely in the bracket *J* which carries it. This bracket is adjustably fixed by a kinematic clamp to the tripod stand *K*, which is provided with levelling screws.

FIG. 1.

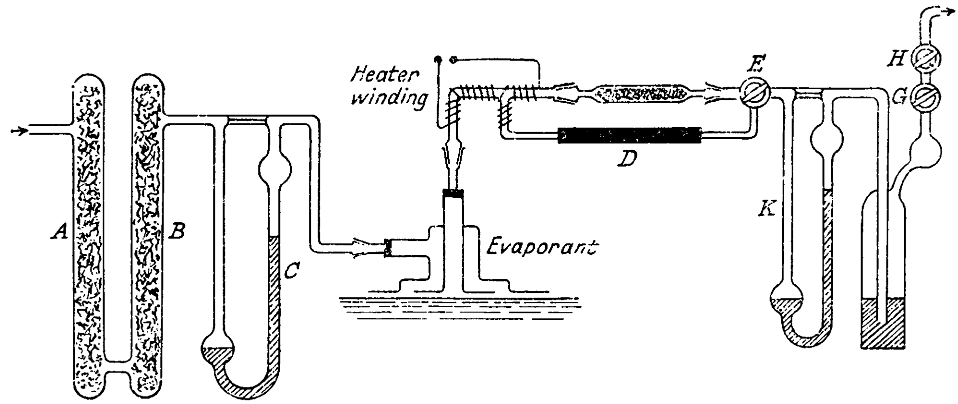


To ensure that the plate *A* is parallel to the water surface, the whole evaporant is rotated about its vertical axis by turning the boss *H*, and the levelling screws at the base of the stand are adjusted until the tip of *E* just touches the surface in all positions. Once this adjustment has been made, the evaporant may be raised or lowered by turning the screw-head, or may be swung out of the way for cleaning the surface by swivelling, and yet can easily be returned precisely to its original relationship to the surface. Satisfactory results were obtained when the distance of the plate *A* from the water surface was exactly 3 mm.

To prevent condensation of water on the inside of the evaporant when the laboratory temperature fell much below 20°, the temperature of the experiments, the evaporant was surrounded by metal tubing through which water at a temperature of 22° constantly circulated from a thermostatically controlled reservoir.

To ensure as constant a temperature as possible for the surface of the water, a thermostatically controlled trough was used. This was a shallow tray of brass (25 cm. × 50 cm. × 5 mm.) coated with black Bakelite, on to the floor of which, about 2 cm. from the sides, strips of 5 mm. square cross section were soldered to form the sides of the trough, which is thus surrounded by a shallow gutter. At 2 cm. from one end of this trough was a well 6 cm. in diameter and 3 cm. deep, for the surface balance. The tray, suitably weighted with lead strips, was fitted into a large tank, standing on three adjustable legs, which was filled with water and thermostatically controlled. A trough of this type is advantageous in that the water surface, being in a hollow, is well protected against disturbance by air currents. Glass plates slipped over the top of the tray exclude all dust and help to keep the temperature steady. When the water surface in the trough proper is swept clean by chromium-plated brass strips (which are used also as barriers) the excess water and impurities collect in the gutter and are sucked away through a tube connected to a filter-pump. The trough and barriers were coated with paraffin wax. This was believed to be safer than ferric stearate, which has been recommended but was found to dissolve gradually in the water. The general arrangement of the apparatus is shown diagrammatically in Fig. 2. Air from a compressed-air cylinder was dried by passing through tubes *A* and *B*, containing sodium hydroxide and phosphoric oxide, and then passed through a capillary flowmeter *C*, direct to the evaporant. By means of a fine adjustment on the cylinder head, the air-flow was kept constant. The moist air, drawn from the evaporant by a water-pump, passed through a weighed tube, 20 cm. long and $1\frac{1}{2}$ cm. in diam. filled with phosphoric oxide, where the water was absorbed. A coil of resistance wire, electrically heated to about 30° above room temperature, served to avoid condensation of moisture on the cool surface of the glass tubing between the evaporant and the absorption tube. In order to flush the whole circuit before collecting the moisture, the air was by-passed along *D*. By turning the three-way tap *E*, the air was drawn through the collecting tube, whence it passed through a capillary flowmeter *K*, through concentrated sulphuric acid to prevent back diffusion from the water-pump, through two taps *G* and *H* to ensure very accurate regulation of the rate of flow, and finally into a 20-litre carboy and so to the water pump. Since the determinations were comparative, the conditions were carefully standardised. Dry air was fed at about 4 l./min., and moist air was drawn from the evaporant at a fixed rate of 2 l./min. ± 15—20 c.c.; the water surface was held at 19·5° and water vapour was collected for $7\frac{1}{2}$ mins. in each run, giving convenient magnitudes of evaporation, *e.g.*, 0·11 g. from a clean water surface. The apparatus was flushed for 2 mins. before each determination. These rates of flow gave a safe margin of excess air, as a blank experiment in which the evaporant was placed over a glass plate in laboratory air almost saturated with water vapour showed that the error due to back diffusion of moist air into the evaporant could not exceed 1% of the total water obtained from a clean water surface. Another blank experiment in which no current of dry air was used gave for the water collected a figure 10% above that obtained when dry air was fed to the evaporant and so proved that the air passing out of the evaporant during an experiment was still unsaturated, an essential condition for the success of the method.

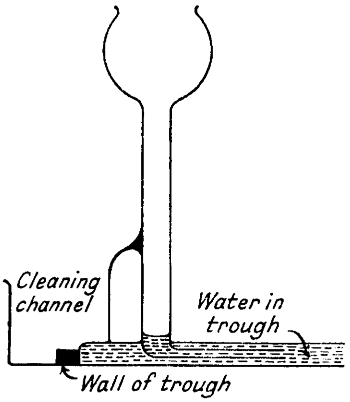
FIG. 2.



Having regard to such obvious potential sources of error as the effects of diffusion and eddying and the difficulty of maintaining constant temperatures under conditions of fairly rapid evaporation, it is satisfactory that the results of separate experiments with a clean water surface did not differ by more than ± 2%. As the observed effects of surface films greatly exceeded this small experimental error it seems clear that the method is adequate for its purpose. Since high velocities of air across the surface might conceivably disturb a film and so produce false results, it is important to remark that under the conditions used the linear velocity of the air was not high, varying from 6 cm./sec. at the periphery of the disc *A* to 40 cm./sec. at the entrance to the central tube *B*, and caused only a very slow motion of minute particles floating on a free water surface. These facts, together with the coherent and reproducible character of the measurements on films, seem to preclude any idea that mechanical disturbance of the films by the air current could have had any appreciable influence on the observed effects. Indeed, the fact that some films almost completely stopped evaporation while others had practically no effect on it seems conclusive on this point.

The surface balance used was the modification of the Wilhelmy surface-tension balance described by Harkins and Anderson (*J. Amer. Chem. Soc.*, 1937, **59**, 2189). It consisted of a microscope slide, at right angles to which at one end a portion of another slide about 1″ square had been sealed to act as a damper. The slide was suspended from a small balance pan which hung from one arm of a balance, to the pointer of which a galvanometer mirror had been attached. Any displacement of the balance was measured by an optical lever. The slide was suspended so that it was half immersed in the water in the well of the trough, and the balance was adjusted by a counterpoise until it was in equilibrium. The weight of the slide was balanced by the upthrust of the water plus the surface tension. Any alteration of the surface tension resulted in a movement of the slide until the new upthrust just balanced the changed surface force. The slide was calibrated by putting weights on the pan equal to the largest force to be measured, and then gradually removing the weights while noting the deflection of the spot of light reflected from the galvanometer mirror on a scale 1 m. away. In these circumstances, a change of surface tension (or a surface pressure) of 1 dyne/cm. gave a deflection of about 5 mm.

Fig. 3.



Harkins and Anderson have claimed that this method is as accurate as the Langmuir–Adam surface balance, and it has the decided advantage that as there are no floating barriers, there is no possibility of the measurements being affected by leakage past them. It must be emphasised, however, that the satisfactory working of this type of balance depends upon the constancy of the contact angle between the slide and the water. For pure water against clean glass, this may safely be taken as zero, and the same assumption may be made when a film covers the water under low surface pressure. For some films under high compression, however, there is a danger that films may build up on the glass, with consequent change in contact angle and complete failure of the balance. For this reason, a careful watch had to be kept on the line of contact; in bright illumination it was easy to observe when the contact angle was no longer zero. Films of alcohols, even under high pressures, behaved well, and did not alter the contact angle, but fatty acid films were less reliable, and the dangerous range of pressure became lower as the chain length increased. This difficulty was partly overcome by ensuring that measurements were always made with the slide emerging from the water, giving a receding contact angle, but in spite of this the absolute values of the higher pressures for the higher fatty acids must be viewed with caution.

To secure constancy of contact angle it was of the utmost importance to ensure that the slide was perfectly clean and it was therefore always kept in chromic–nitric acid cleaning mixture when not in use. It was found that the best way to clean the slide once films had built up, was by washing it first in absolute alcohol, and then at once in chromic–nitric acid mixture. When so treated the slide was immediately ready for use again.

Because the balance records only differences of surface tension between pure water and water with a film on it, every experiment began with the slide dipped into clean water, and the zero reading on the balance was taken before the film was added. Changes of level (which would, of course, change the zero) were avoided by means of the device shown in Fig. 3, which was immersed in the trough and clamped so that the fine pointer, made of blue glass, just touched the surface of the water. When water evaporated, the level was readjusted to the pointer by adding water through the funnel : as the water entered below the surface, it did not affect the film.

Except for the proteins, the film-forming substances were spread from dilute benzene solution. The benzene was prepared by shaking crystallisable benzene with concentrated sulphuric acid and then with sodium hydroxide, drying it over sodium, and finally distilling it in a vacuum at room temperature. Such benzene was free from all surface-active substances, though it still spread on water. Its purity was verified by spreading several drops on clean water between two barriers : on bringing the barriers together no deflection of the balance was noted. The purity of the film-forming substances was checked by m. p. determinations. The films were spread by the usual method between two barriers on the clean surface of water maintained at p_H 7·0, care being taken always to ensure that the film present was less than was necessary to cover the surface completely with a monolayer. By slowly moving up one barrier the film was gradually compressed, and when the pressure was relatively steady, the evaporant was put in position over the film and a run was commenced. At low pressures the pressure remained comparatively steady, but at higher pressures there was a definite fall in pressure during a run, and the pressure recorded for the run was the mean of the initial and final values. This fall in pressure, which is not due to leakage, is fully discussed in the following communication. For some films at high pressures, the drift in pressure became so rapid as to impose a natural limitation on the pressures to which the survey could be extended.

The quantity of water, q_2, evaporated in a given time through a film, compared with the quantity, q_1, evaporated in the same time under identical conditions from a clean water surface was expressed as a percentage, Q, and values of Q were determined at various surface pressures. The table gives a typical series of data obtained with *n*-docosanol, the substance which permitted determinations over the widest range. These results and corresponding series of values for acids and alcohols are summarised in the curves recorded in Figs. 4 and 5 respectively. In drawing these curves numerous points which lie along the 100% line have been omitted for the sake of clarity.

Pressure, dynes/cm.	0	3	7·7	9·7	13·3	16·2	23·0	33·0	42·0	48·0
Quantity of water evaporated, g. ...	0·114	0·110	0·101	0·089	0·045	0·027	0·020	0·017	0·009	0·001
$Q = 100q_2/q_1$	100	96	88	77	39	23	17	14	9	1

From the curves it is at once apparent that the resistance offered by surface films to the evaporation of water is an interesting and significant property, the magnitude of which depends upon the nature of the film and is, in most cases, very largely influenced by change of surface pressure. On further consideration it is seen that the resistances of the several films cannot be correlated with their physical states. Cetyl alcohol, for example, gives what is generally regarded as a liquid film, even though it is condensed at pressures above about 7 dynes/cm.; egg albumin, on the other hand, is generally regarded as giving a solid film, because the molecules have sufficient lateral adhesion to prevent ready diffusion. Yet albumen has no measurable effect on evaporation, even when compressed to 21 dynes/cm.; whereas above 22 dynes/cm. cetyl alcohol produces a marked reduction. It should be explained that, as the albumin film is very compressible, the size of the trough did not permit measurements above a pressure of 21 dynes/cm. with this substance.

From the information at present available, it seems that the effects of films in diminishing the rate of evaporation of water from a surface fall into two classes differing considerably in their order of magnitude : first, the effects noted by Rideal, occurring at low surface pressures, which are so small that they fall within the normal error of experiments with the evaporant; and secondly, the relatively very large effects with which the present experiments are concerned.

The latter effects are highly specific : inappreciable for some substances, quite large for others. Also they are observed only above a critical surface pressure which appears to be characteristic for each substance. A curious feature of this resistance, for which no explanation can yet be offered, is that it rises to a considerable magnitude, and does so rather suddenly, at a surface pressure much beyond that at which the film loses its initial compressibility. It might have been expected that when the molecules in the film become so closely packed as to allow of little further compression the resistance of the film to the passage of water would approach a maximum value, but this is not the case. For example, examination of the force–area curves obtained by previous authors shows that stearic acid becomes relatively incompressible on alkaline solution at a pressure of

3 dynes/cm., and on fresh distilled water at 15 dynes/cm.; yet such films offer no substantial resistance to evaporation at pressures less than 20 dynes/cm. Cetyl alcohol becomes incompressible at about 6 dynes/cm., yet again there is no material resistance to evaporation below a pressure of 20 dynes/cm. Cholesterol, which gives a practically

FIG. 4.

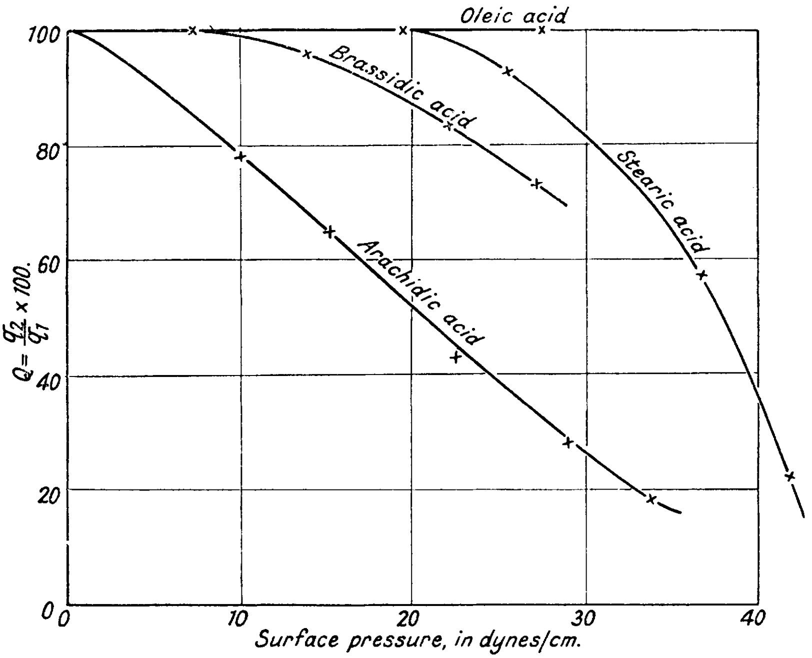
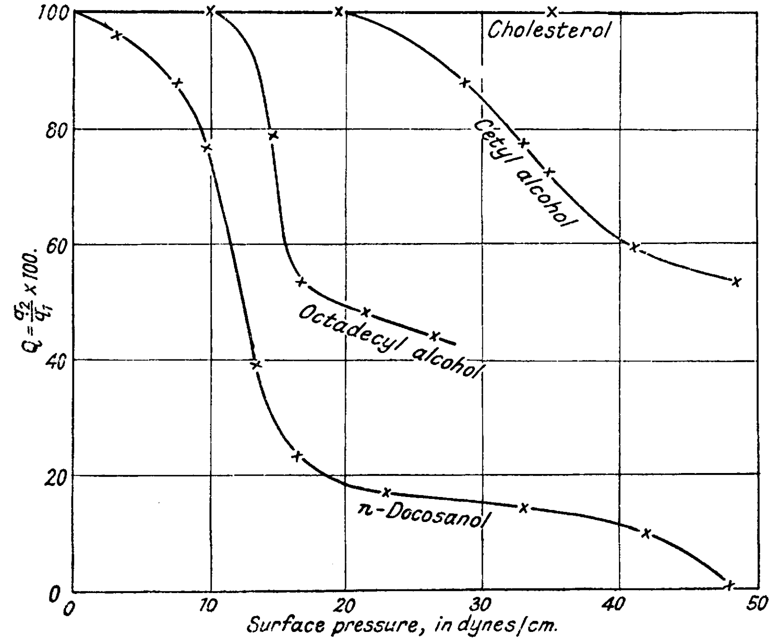


FIG. 5.



incompressible film at very low pressures, offers no resistance at all to evaporation even at a pressure of 35 dynes/cm.

It appears that the effect of hydrophilic groups in the chain is to increase the ease with which water molecules escape. It is found, for example, that proteins and the unsaturated acids, oleic and elaidic, show no resistance. Increased length of chain lowers the pressure at which the resistance effect is first observed, as is demonstrated by comparing the curves for arachidic and stearic acids, and also for the three alcohols, docosanol, octadecyl alcohol, and hexadecyl alcohol. The effect of the long chain in brassidic acid is partly counteracted by that of the hydrophilic double bond in the chain; hence its intermediate position.

The curves afford an obvious explanation of the apparently anomalous behaviour of cetyl alcohol reported by Langmuir and Langmuir, and show why these authors did not notice that the resistance of stearic acid may be even more marked than that of cetyl alcohol. All previous workers used films in equilibrium with excess of the film-forming material. Under these conditions stearic acid does not give a pressure large enough for the resistance to be important. In this way Rideal obtained a surface pressure of 5 dynes/cm. at 25° for stearic acid; by spreading it from a benzene solution, we have obtained a pressure of about 20 dynes/cm., which is thus very near, but still below, the critical pressure. Cetyl alcohol, however, spreads to give naturally a surface pressure of over 40 dynes/cm., which is well beyond the critical value, and it was for this reason that Langmuir and Langmuir were able to notice its exceptional behaviour. Adam (" The Physics and Chemistry of Surfaces," 1938, p. 104) has drawn attention to the curious order of the resistance noticed by Rideal, who found that stearic, lauric, and oleic acids reduced evaporation in a vacuum at 25° by 28·1, 42·4, and 52·5% respectively. It seemed strange that lauric acid, having a shorter chain than stearic acid, should have a more marked resistance, and that the expanded film of oleic acid should have a greater resistance than the condensed film of stearic acid. If, however, the assumption is made that there is a definite relationship for any particular film between the surface pressure and the resistance, even with respect to this small effect, Rideal's results are quite reasonable, as he worked with surface pressures of 5, 26·3, and 29·1 dynes/cm., for stearic, lauric, and oleic acid respectively.

The data as yet available are inadequate to suggest a clear conception of the way in which a film hinders evaporation. The fact that the resistance becomes really marked only at high pressures may perhaps be explained by assuming that the surface layer contains water in addition to the film-forming substance. It may be that, in considering the properties of surface films, it would be generally useful to regard the films as a solution of water in the film-forming substance, in equilibrium with a solution of the film-forming substance in the water substrate. This suggestion is amplified in the following communication, where it is used to explain why surface pressure is so important a factor in solubility. If it be assumed that the effect of increasing the surface pressure is to squeeze water molecules back into the substrate, then, since there are fewer water molecules in the surface, the rate of evaporation would be reduced. On this view, hydrophilic groups in the chain would increase the solubility of water in the film, and hence reduce the resistance so that a higher pressure would be required to get the effect observed at a lower pressure with a film of the same chain length but without the hydrophilic groups in the chain. The difference, of the order of 10%, found between the cross-section of the molecule as calculated from force–area curves and as calculated from X-ray data may possibly be explained by the presence of water molecules trapped in the film, rather than by the tilting of the molecules, which has been suggested.

It is of interest to record that the same technique was used to investigate how a relatively thick film of lubricating oil (of the type called " indicator oil " by Langmuir) affects the evaporation. It was found that a film just thick enough to show the first interference colours had a Q value as high as 97%, and even when the film was so thick that interference colours could no longer be seen, the Q value was still 27%. This is remarkable, and shows that a greater resistance to evaporation can be obtained with a closely packed film one molecule thick than with an indicator oil film of the order of 100 molecules thick. It is hoped that further work may afford some explanation of this curious fact.

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