23. *A New " Ageing " Phenomenon in Unimolecular Films on Water.*

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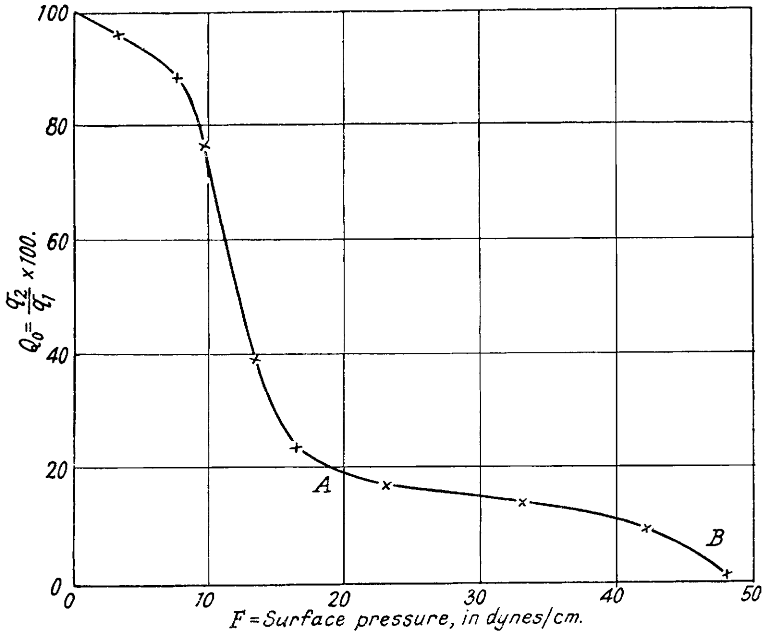
In applying the technique of the " evaporant," already described (this vol., p. 106), to comparative determinations of the rate of evaporation of water into an air current from free and from film-covered water surfaces, an " ageing effect " has been discovered whereby compressed films, *e.g.*, of *n*-docosanol or arachidic acid, which when freshly formed and compressed largely reduce the rate of evaporation from the water surface, become much more permeable to water if they are first allowed to lie for some time on the water surface, especially if the ageing is effected at a relatively low surface pressure. The magnitude of the ageing effect varies directly with time of ageing and inversely with the surface pressure during ageing. A film of *n*-docosanol when freshly formed and compressed to a surface pressure of 47 dynes/cm. reduces evaporation to about 2% of that from the clean water surface; if, however, the film is aged on the water surface at zero pressure for 20 hours and then compressed to 47 dynes/cm., the evaporation through it exceeds 95% of that from the free water surface.

The phenomenon is explained on the hypothesis that in an uncompressed film the single molecules, being in active motion and free to associate, gradually do so in pairs, forming double molecules having a hydrophilic alcoholic group at each end, which, being thus akin to the single molecules of dihydroxy-alcohols, lie and remain flat upon the water surface and so greatly enhance the permeability of the film to water. In accordance with this hypothesis, it is found that a film, when compressed after being aged at low pressure, occupies a substantially greater area than when compressed to the same pressure before ageing, and is also more soluble.

IN describing the reduction of the rate of evaporation of water produced by unimolecular films spread on its surface (this vol., p. 106), we showed that the resistance to evaporation exhibited by any given film when freshly formed varies with the surface pressure. During the investigation, however, it sometimes happened that the quantity of water evaporated exceeded that required by this simple relationship. Further examination of these anomalous effects has shown that the resistance of a film to evaporation depends, not only on the surface pressure at the time of measurement, but also on the time during which the film has been spread prior to the measurement and on the surface pressure at which it has been kept.

For the investigation of this phenomenon *n*-docosanol is especially suitable because it is very sparingly soluble and, therefore, permits the change of resistance with surface pressure and with time to be explored over a wide range. Also, because of its long hydrocarbon chain, it shows, at moderate and high surface pressures, a very marked reduction in the rate of evaporation. It seems very likely, however, that the effects of duration and conditions of keeping prior to measurement, which may conveniently be called the "ageing effect," are common to all films which show a high resistance to evaporation, even though, for reasons indicated below, they cannot always be observed.

The apparatus and technique were exactly as described in the previous paper. By plotting Q_0, the evaporation through the freshly formed and compressed film expressed as a percentage of that from a clean water surface under the same conditions, against F, the surface pressure, the curve shown in the figure was obtained. Because of the large reduction of evaporation there, the region AB was found to be most suitable for observing the ageing effect. By means of the "evaporant," the values of Q were now determined at various values of the surface pressure on films which had been spread and kept at various constant surface pressures for various periods of time, t, and these values (Q_t) may be compared with the values of Q_0 at the corresponding surface pressures. A typical series of results for *n*-docosanol is given in the following table. From these it is immediately



Surface pressure during ageing, dynes/cm.	Duration of ageing = t hrs.	Surface pressure of evaporation expt. = F dynes/cm.	Q_t.	Q_0.
0	1	17	45	21
0	1	32	39	13
0	2	42	79	9
4	14	32	66	13
16	1	16	63	27
16	2	16	80	27
16	3	16	89	27
16	19	16	100	27
16	21	47	84	1
17	18	47	58	1
23	3	23	44	16
23	6	23	53	16
23	9	23	59	16
47	20	47	4	2

apparent that ageing always increases the evaporation through the film and that under favourable conditions this increase may be very large. On comparing measurements made at the same surface pressure, it is clear, also, that the increase in transmission of water through the film, *i.e.*, the ageing effect, varies in magnitude directly with the time of ageing and inversely with the surface pressure during ageing. The most striking effect is obtained by ageing at zero pressure: by spreading insufficient docosanol to form a complete monolayer from benzene solution on a water surface, and then after 1—2 hours measuring the value of Q_t at a high surface pressure (42 dynes/cm.), it is found that the transmission of water through the film is about ten times that through a film freshly formed and compressed to the same surface pressure. If the film is left standing under slight compression, the increase of Q_t with time is less marked, but still definite. If the film, when formed, is compressed to a value near *B*, *i.e.*, about 45 dynes/cm., and so left to stand, the ageing effect is very slight and is only apparent after at least 20 hours. The evaporation of water through such a film, whether fresh or aged, is only 2—3% of the evaporation from a free water surface. On the other hand, if the film is left uncompressed for 20 hours, and is then compressed to 45 dynes/cm. for measurement, it is found to produce no measurable reduction at all in the rate of evaporation from the water surface.

The explanation of this remarkable phenomenon is by no means obvious. The facts last cited above seem to militate against any idea that ageing may be due to a break up of the film: on the contrary, it appears that the waterproof character of a *compressed* film is permanent. Since compression hinders ageing, it seems improbable that ageing can be attributed to any change in the hydrophilic group, for that end of the molecule is, presumably, always equally in contact with water whether the film be compressed or uncompressed. Any idea that ageing might be due to oxidation of the alcoholic group appears to be excluded by the fact that arachidic acid exhibits the phenomenon. It seems therefore, that the explanation must depend upon the properties of the hydrophobic carbon chain; yet, on the other hand, the idea of simple hydration of this part of the molecule, even if otherwise unobjectionable, will not suffice, because it does not explain why the process takes time and is, indeed, very slow.

Considering all the facts given above, we incline to the hypothesis that in an uncompressed film on water there occurs a slow, progressive, and possibly reversible association of the film-forming molecules. When in an uncompressed film, the molecules of the alcohol lie flat on the surface of the water and are at the same time kept in active motion by the movement of the water molecules. It is therefore conceivable that occasionally two alcohol molecules may meet in such a way that they join to form a double molecule, probably meeting head-to-tail and broadside on, so that the hydrophilic groups are at opposite ends of the double molecule. This molecule in its surface-film behaviour would resemble a dihydroxy-alcohol rather than the simple alcohol from which it is derived, and so would tend to lie flat on the surface, even in the compressed film.

Whether the variation in the rate of transmission of water with surface pressure is (as suggested in the earlier paper) dependent upon the amount of water dissolved in the surface film, or whether it is merely a question of the packing of the film, the presence of associated molecules of this kind might be expected to increase the transmission. On the former view it seems not improbable that the film containing the di-molecules (each having an extra hydrophilic group) would dissolve more water than would the film of single molecules, and on the latter view it might reasonably be assumed that a molecule lying flat on the surface will constitute a water-permeable gap in a body of molecules standing upright.

The hypothesis here outlined is supported by the observation that if a compressed film of docosanol is left standing for some time, a small but definite rise in surface pressure occurs, as might be expected from the formation of molecules having enhanced hydrophilic properties. In the preceding paper it was shown that the surface pressure of cetyl and octadecyl alcohols falls considerably with time, and this fall was ascribed to the effect of solution. Docosanol, because of its longer chain, is much less soluble, and therefore permits the rise in pressure during ageing to become apparent. This rise of pressure is only about 1 dyne/cm. in 3 or 4 hours, and so is much smaller than the fall in pressure in the case of cetyl alcohol due to solubility. A rise in pressure due to ageing probably occurs with cetyl alcohol as with docosanol, but it is completely masked by the larger fall in pressure due to solution.

Further tests of this hypothesis, and additional information on the general question of ageing could probably be secured by measuring force–area curves or surface potential changes. It seems possible, indeed, that some of the results recorded by Addink (*J. Chem. Physics*, 1934, **2**, 574) show the effect of ageing.

One direct and simple test of our hypothesis, however, could easily be applied under our experimental conditions. If ageing involves, as we have supposed, the conversion of a substantial proportion of the molecules in the film into double molecules which will persist in lying flat on the water surface, a given weight of film-forming material at a given moderate surface pressure should occupy a larger area after ageing than before. On applying this test to docosanol it was found that the ratio of area to mass at constant surface pressure was, in fact, substantially increased by ageing, and that the film had become more soluble. In a typical case a film of docosanol, having an area of 200 sq. cm. at 2 dynes/cm. when freshly formed, had, after ageing for one hour at zero pressure, an area of 220 sq. cm. at 2 dynes/cm., and after 3 hours an area of 260 sq. cm.

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