

*Some Surface Properties of Docosyltrimethylammonium Bromide,  
and of Docosane-1-sulphonic Acid and its Sodium Salt.*

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The effect of docosyltrimethylammonium bromide, and docosane-1-sulphonic acid and its sodium salt on the rate of evaporation of a water substrate has been investigated and the effect of the sulphonic acid found to be appreciable.

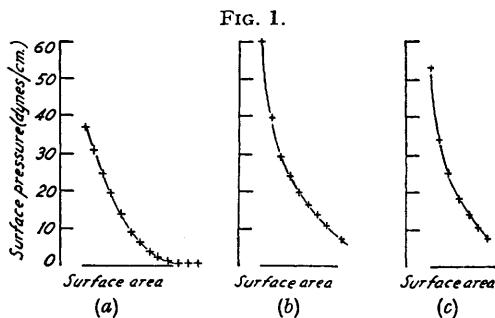
AVAILABLE evidence suggests that, for a monolayer spread on water to be effective in reducing the rate of evaporation of the substrate appreciably, it must consist of an unbranched long-chain hydrocarbon and a strongly polar, small head group, and be compressed to the condensed phase. So far, the longest hydrocarbon chain investigated has been that in docosanol (Sebba and Briscoe, *J.*, 1940, 106). Longer chains could not easily be investigated as the alcohols and acids of higher homologues do not spread easily. In the search for a spontaneously spreading substance that would form a monolayer which, without external compression, would have an appreciable effect on the rate of evaporation of water from open surfaces, it was decided to investigate the long-chain sulphonic acids and their salts, whose surface properties have not yet been examined. These substances

show considerable surface activity up to  $C_{18}$ , but molecules of this length are too soluble in water to give a durable monolayer. As a preliminary, a  $C_{22}$  sulphonic acid and its salt and the  $C_{22}$  quaternary ammonium salt have been synthesised and investigated.

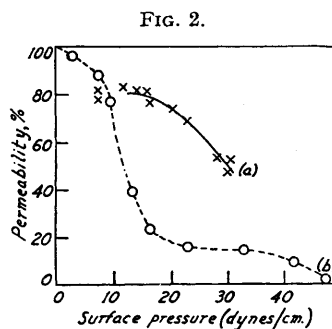
#### EXPERIMENTAL

Erucic acid from rape-seed oil (*Org. Synth.*, Coll. Vol. II, p. 258) was esterified, and the ester reduced (Adams's catalyst) to ethyl behenate. This, by a modified Bouveault-Blanc reaction, butanol being used in place of ethanol, yielded docosan-1-ol. The corresponding bromide when heated with sodium sulphite at  $200^\circ$  (Strecker, *Annalen*, 1873, **168**, 145; Reed and Tartar, *J. Amer. Chem. Soc.*, 1935, **57**, 570) afforded sodium docosane-1-sulphonate which separated from ethanol as a white crystalline solid (Found: C, 64.3; H, 11.1.  $C_{22}H_{46}O_3SNa$  requires C, 64.2; H, 10.9%). It is insoluble in cold water but soluble in hot water, from which it is precipitated on cooling in either crystalline or gelatinous form; it is practically insoluble in hexane, benzene, ether, or chloroform.

Dry hydrogen chloride was bubbled into a suspension of the sodium salt in benzene, heated under reflux, to liberate docosane-1-sulphonic acid. After 2 hr. the residual solid was filtered



(a) Docosyltrimethylammonium bromide.  
(b) Docosane-1-sulphonic acid.  
(c) Sodium docosane-1-sulphonate.



(a) Docosane-1-sulphonic acid.  
(b) Docosan-1-ol.

off, and the filtrate shaken twice with water to remove hydrochloric acid; the layers were separated by centrifuging. Removal of the benzene by distillation under reduced pressure left a white, waxy solid, easily decomposed by heat (even at  $60-70^\circ$  *in vacuo*), moderately soluble in hexane and benzene. It is insoluble in cold water, but when heated forms a clear solution from which it sets to a gel on cooling.

When heated with trimethylamine at  $100^\circ$  for 24 hr. in a sealed tube, docosyl bromide was converted into docosyltrimethylammonium bromide (*J. Biol. Chem.*, 1924, **59**, 905) which was recrystallised several times from acetone-ethanol. The solid decomposes below its m. p. (Found: C, 67.1; H, 12.2. Calc. for  $C_{25}H_{54}NBr$ : C, 66.9; H, 12.1%).

The surface-pressure-area curves were determined in the usual way, by means of a Langmuir-Adam trough and a floating-barrier surface balance. The change in resistance to evaporation with change of surface pressure was measured by Sebba and Sutin's method (*J.*, 1952, 2513).

*Results.*—The most satisfactory solvent from which to spread the docosyltrimethylammonium bromide was chloroform. Being denser than water, the chloroform had to be placed on the surface very carefully in which case a satisfactory film could be obtained, which on distilled water had an equilibrium pressure of 28.4 dynes/cm. Owing to the slight solubility of the monolayer, the absolute values of the area occupied per molecule could not be determined, and Fig. 1 (a), only shows the shape of the  $F-A$  curve. At pressures above 30 dynes/cm. the solubility of the film was so great that no reliable measurements could be made. For the same reason, it was not possible to determine the effect on evaporation at high pressures. At a surface pressure of 23 dynes/cm., the permeability was found to be 97%, and at 27 dynes to be 87%. The resistance to evaporation offered by this film, even when condensed, is therefore, not very marked.

Sodium docosane-1-sulphonate is insoluble in all common organic solvents except ethyl alcohol. In spite of the obvious disadvantages of a soluble polar solvent, there was no alternative to spreading it from a hot solution in ethyl alcohol, to which sufficient benzene had been added to make the solution partially immiscible with water, but not enough to precipitate the salt. It was difficult to study the surface characteristics of this substance satisfactorily, as owing

to solubility, the surface pressures were never steady, but decreased continuously, a phenomenon noticed with some other films by Sebba and Briscoe (*J.*, 1940, 114). A pseudo-equilibrium pressure of 30 dynes/cm. was obtained. Even a substrate containing  $Ba^{++}$  ions did not depress the solubility, in spite of the fact that barium sulphonates are generally less soluble. This difficulty made determination of an exact  $F-A$  curve impracticable, therefore Fig. 1(c) shows only the general shape of the curve. Nor could a complete study be made of the change of evaporation through the film with change in pressure. However, at an approximate surface pressure of 20 dynes/cm., the permeability was found to be 72%, and at 28 dynes/cm. it was 54%. This indicates that at pressures in excess of 28 dynes/cm., the resistance to evaporation offered by the monolayer would be considerable.

Docosane-1-sulphonic acid is soluble in benzene, and was, therefore, spread from a benzene solution. It is unfortunate that as the sulphonic acids are relatively strong, the possibility of slight contamination with the sodium salt which is slightly soluble in benzene could not be entirely excluded. This monolayer also showed slight solubility, as indicated by the fall of surface pressure with time. A pseudo-equilibrium pressure of approximately 11 dynes/cm. was found, but the true equilibrium surface pressure may be somewhat greater. The monolayer appeared to be an elastic solid at that pressure. Again, owing to the solubility of the monolayer, the value of the molecular cross-section could not be obtained, but only the general shape of the  $F-A$  curve, plotted against a relative area. In the determination of the effect of surface pressure on the rates of evaporation, the solubility imposed limits at both ends of the curve. It prevented determinations at pressures higher than 30 dynes/cm. as the film was too unstable and dissolved too rapidly. On the other hand, since the pressure in the film represents an equilibrium between dissolved substance and its monolayer, the reduction of the pressure below 7 dynes/cm. led to gradual penetration of the film by dissolved substance with a corresponding increase in the surface pressure. It can be stated unequivocally that this rise was not due to impurities in the trough, as no such rise was observed before the sulphonic acid was spread on the water. The substrate used was a borate buffer at pH 7. Changing the substrate to pH 2 had no appreciable effect on the solubility of the film. The relation between rate of water permeability and surface pressure is shown in Fig. 2.

It will be noticed that, when the surface pressure is increased beyond 17 dynes/cm., there is a marked reduction in rate of water evaporation. A puzzling feature, however, is that the permeability appears to be relatively constant at 80% between pressures of 7 and 17 dynes/cm., whereas it would be expected to rise steadily towards 100% permeability [the continuous line (a) in Fig. 2 should be continued to the left]. This is not an obvious experimental error, as the experiment was repeated, though the possibility of a small amount of a more impenetrable impurity in the monolayer cannot be excluded. A similar plateau, though associated with much more marked evaporation resistance, is shown by docosan-1-ol, and its curve (taken from Sebba and Briscoe's paper, *loc. cit.*) is shown, for comparison, in Fig. 2 as broken lines. If the phenomenon is real, it would be profitable to synthesise a similar acid with two or more additional carbon atoms in the chain, for the solubility effect should then be less serious.

The Table summarises the relative effect on permeability of various monolayers of approximately the same chain length at approximately the same surface pressures.

Compound	Surface pressure, dynes/cm.	Permeability, %
Docosyltrimethylammonium bromide .....	27	87
Sodium docosane-1-sulphonate .....	28	54
Docosane-1-sulphonic acid .....	28	55
Arachidic acid * .....	28	31
Docosan-1-ol * .....	28	15

\* Sebba and Briscoe (*J.*, 1940, 106).

From these results it is seen that the order of effectiveness of the end group is  $OH > CO_2H > SO_3^- > NMe_3^+ Br^-$ . The sodium docosane-1-sulphonate seems to have a resistance to evaporation similar to that of the free acid, as is to be expected, for the long-chain anions are identical and the sulphonic acids are relatively strong. The sodium salt has the advantage of a higher equilibrium pressure, so it offers indications that a self-spreading surface-active substance, which will attain of its own accord a surface pressure large enough appreciably to reduce evaporation from open water surfaces, may be found amongst the sodium salts of the sulphonic acids of slightly greater chain-length than the one used in these experiments.