Monomolecular Layers of Chlorophyll

IN order to study the properties of monomolecular layers of chlorophyll, a mixture of the modifications a and b in the proportion $3:1$ (the proportion encountered in living plants), furnished by Prof. Stoll of Basle, was dissolved in ether or acetone. The solution was first added to pure water, to 0·01 normal and to 0·1 normal sulphuric acid. The relation obtained between area and pressure showed that a monomolecular layer actually is formed. No noticeable difference was found between the case of pure water and that of the acid, so that all the results can be incorporated in Curve I (Fig. 1). The spreading with a solution in acetone is recommended because on account of the greater volatility of the ether, traces of solid chlorophyll frequently remain at the opening of the pipette, making it more difficult to obtain reproducible values. Curve I corresponds to a film of the liquid type. The limiting area per molecule at zero compression is 124 A.², a value in satisfactory agreement with the value of about 133 A.², recently given by Hughes[1]. The small difference probably is due to impurities. At a pressure of about 26 dynes per cm. the film becomes polymolecular, the curve becoming a horizontal line.
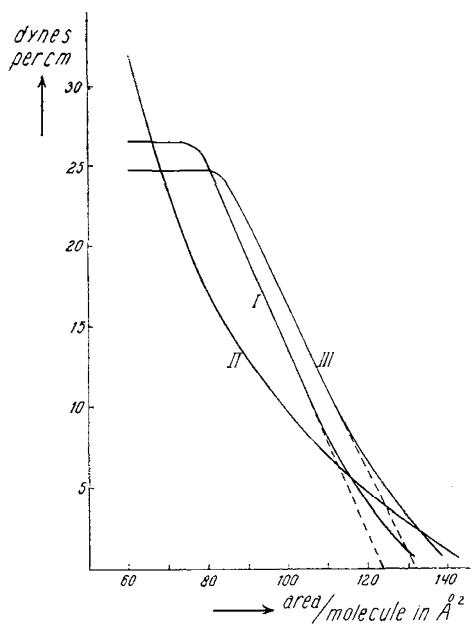

FIG. 1.

As the chlorophyll molecule possesses several double bonds, another curve was expected when spreading on an acid solution of potassium permanganate. This expectation proved to be justified. Curve II was obtained on a 1 per cent solution of potassium permanganate in 0·1 normal sulphuric acid. Over the whole range, but more particularly at small pressures, the film is more compressible than the films previously studied. It was impossible for us to measure the pressure where the film becomes polymolecular, this pressure being too high for registration by the instrument used.

Finally, the behaviour of chlorophyll on water containing carbon dioxide was studied. Great care had to be taken not to have the water oversaturated with carbon dioxide. Ultimately the experiments were carried out on water in equilibrium with

carbon dioxide at one atmosphere. The results are contained in Curve III. The molecule appears to require a greater space under the influence of carbon dioxide, having a limiting area of 132 A.². That this is not due to the acid character of the solution is indicated by the experiments on sulphuric acid. The pressure required to make the film polymolecular is slightly less than in the case of pure water. Experiments with nitric oxide showed that this gas, which in its physical properties (solubility, etc.) strongly resembles carbon dioxide, has no effect.

In conclusion, I wish to express my thanks to Prof. E. Gorter in Leyden for the loan of a Langmuir trough of special construction, which enabled me to work in atmospheres other than air. Also I am much obliged to Prof. Prins for putting at my disposal the sample of chlorophyll and for suggesting the investigation on water containing carbon dioxide, to Dr. J. H. P. Jonxis for valuable advice concerning the technique of the experiments, to Dr. R. de L. Kronig for stimulating discussion and to Messrs. J. Vermeer and F. H. Robaard for their kind help in the performance of the measurements.

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[1] A. Hughes, *Proc. Roy. Soc.*, A, **155**, 710 (1936).

Contact Potentials of Reversible Soluble Films of Lauric Acid

WHEN a nearly saturated solution of lauric acid in distilled water is placed in an Adam-Jessop film-pressure trough, the soluble adsorbed film may be compressed or swept in the same manner as an insoluble film of a higher fatty acid. However, the surface is rapidly replenished by diffusion from below, after sweeping, or the compressed film diffuses downward. In either case the reading of the film-balance returns to zero, in a period of about thirty minutes at 25° C. Similar effects have been noticed with benzopurpurin solutions[1] and with soap solutions[2]. Since the contact potential of solutions is proportional to the concentration of the surface-active solute, simultaneous contact potential measurements with a polonium-covered silver electrode on the above surfaces might be expected to yield potential-time curves nearly parallel to the force-time curves. Such proved to be the case, with the following notable differences.

Referred to a pure water surface as zero, the contact potential of a nearly saturated surface of lauric acid solution is − 120 mv. Upon sweeping rapidly, the surface tension of the swept surface rises about five dynes and returns to its original value slowly. The surface potential immediately after sweeping rises to 0 mv., and falls rapidly to − 100 mv. in twelve minutes, whilst the surface tension has changed but a dyne per centimetre. This result is to be expected, since the first film to be formed by diffusion from below is necessarily dilute, and contributes but a small surface pressure, but a large change in surface potential. After twelve minutes the film becomes more close-packed, and the surface tension falls more rapidly, while the potential changes but slightly, in complete accordance with the results of Harkins and Fischer[3] on lauric acid films spread by the aid of a solvent.