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Electron Micrographs of Monolayers of Stearic Acid

At the second International Congress of Surface Activity held in London during April 1957, we presented results of a study with film balance and electron microscope of monolayers of *n*-hexatriacontanoic acid¹. This compound shows small islands irregular in size and shape at low surface pressures (15 dynes/cm.), a continuous monolayer with discontinuous uncovered areas at intermediate pressures (25 dynes/cm.), a continuous homogeneous monolayer at high pressures (40 dynes/cm.), and long flat structures two molecules thick after collapse.

Monolayers of other compounds have since been examined: stearic, arachidic, *n*-hexacosanoic and *n*-dotetracontanoic acids give, as expected, monolayer structures much like those of *n*-hexatriacontanoic acid; *n*-octadecyl alcohol and cholesterol show related structures. Of principal interest is the behaviour of stearic acid at low surface pressures. It is the classical compound in monolayer research; but because of the small thickness of its monolayer it is more difficult to study in the electron microscope than *n*-hexatriacontanoic acid.

Monolayers of stearic acid were successfully transferred from the film balance at surface pressures as

Fig. 1. Monolayer of stearic acid at 3 dynes per cm.

Fig. 2. Monolayer of stearic acid at 10 dynes per cm.

low² as 3 dynes per cm. An electron micrograph of such a sample is shown in Fig. 1. The direction of shadow-casting is indicated by an arrow; shadows appear as light areas. Many small islands, irregular in shape and about 1000 Å. in diameter, are observed. Shadow widths establish that the islands are about 25 Å. or one molecule thick. Close examination reveals that the spaces between islands actually contain many small structures. Presumably, smaller aggregates and individual molecules beyond the limit of the electron microscope may also be present.

At greater surface pressures, less area remains uncovered. Fig. 2 is an unusual micrograph of a stearic acid monolayer transferred from the film balance at 10 dynes per cm. Most striking is the circular geometry of many of the islands, diameters of which range from 3000 to 50,000 Å. In related monolayer studies, approximately circular islands, circular holes, and circular platelets on top of monolayers have been observed.

Circular islands that resemble flattened liquid droplets are somewhat surprising when one considers that the melting point of stearic acid is 69° C. and that the experiments were conducted at 25° C. However, forces at an edge of a 'two-dimensional' monolayer may be analogous to forces in the surface of a 'three-dimensional' system. Just as spheres with minimum surface energy appear in bulk liquid systems, circular disks may be expected in monolayers with sufficient mobility. Possible effects of droplets forming in the water film sandwiched temporarily between the monolayer and the collodion support used in transfer must also be considered; new transfer techniques now under study may resolve such effects. Experiments at higher temperatures should help define the role of surface mobility in the formation of monolayer islands.

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¹ Ries, jun., H. E., and Kimball, W. A., Proc. Second Internat. Cong. Surface Activity, 1, 75 (Butterworths Scientific Pub., London, 1957). See also Ries and Kimball, *J. Phys. Chem.*, 59, 94 (1955).

² For the complete pressure-area isotherm, see Ries, jun., H. E., and Cook, H. D., *J. Colloid Sci.*, 9, 535 (1954).