violet before adding the reductant. Otherwise there is no visible change on reducing the dye to the semiquinone state.

FROM THE LABORATORIES OF
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Polymolecular Films

BY WILLIAM D. HARKINS AND ROBERT J. MYERS

Surface films which spread over water are supposed to be monomolecular. However, Harkins and Morgan[1] were able to produce solid, partly crystalline films with a mean thickness much greater than this. Thus to a spreading substance whose organic molecules contain a polar group (stearic acid, etc.) they added a thickening or nonpolar substance (phenanthrene). In the present work polymolecular liquid films were produced by thickening the films with a liquid paraffin oil (nujol) of low volatility.

1. Condensed Films.—Films of pure stearic acid form condensed films on 0.01 N hydrochloric acid at room temperature except at pressures below about 0.2 dyne per cm. The addition of 1.61 g. of nujol to 1 g. of stearic acid in the film forming substances does not seem to increase the area of the condensed film (Fig. 1, expts. 91 and 110), but only weakens it at high pressures.

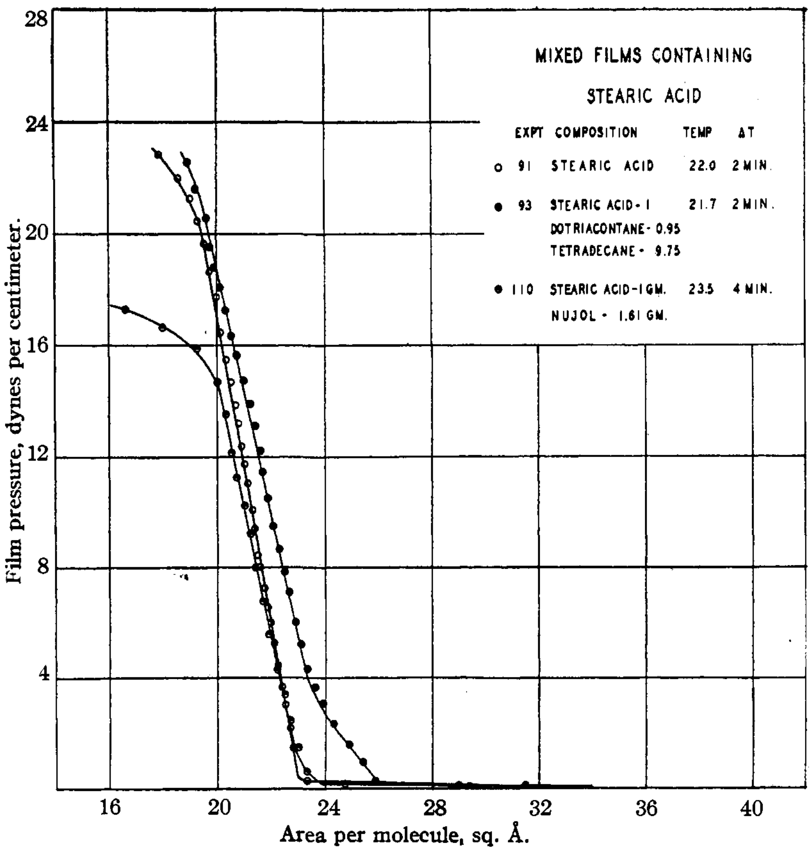

Fig. 1.—Poly- and mono-molecular films with stearic acid.

The areas given in the figures of this paper represent the area per molecule of the more polar constituent (stearic acid, etc.).

2. Expanded Films of Oleic Acid.—The effects are, however, markedly different in cases in which the acid when alone forms an "expanded" film, as in the case of oleic acid (Fig. 2). Here the mixed film contains 1.66 parts by weight of the paraffin oil to 1 part of oleic acid. The effect of the paraffin oil is very great, since it raises the surface pressure greatly at large areas, and decreases it very markedly at low areas. At 36.4 sq. Å. per molecule of oleic acid the pressures are the same for the pure acid and the mixture.

3. Expanded Films of Myristic Acid.—At 22.8° films of pure myristic acid exhibit a kink in the curve at an area of 25.45 sq. Å. and a pressure of 17.25 dynes per cm. The addition of 1.67 parts

(1) Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 631 (1925).

by weight of nujol to 1 part of myristic acid removes the kink and increases the film pressure at any given area. The increase is particularly great at the lower pressures (larger areas). With a greater proportion of nujol (9.08 parts) the phenomenon encountered with oleic acid is found, that is, the paraffin oil increases the pressure at large molecular areas and decreases it at the lower areas. The decrease in surface pressure at the lower areas becomes much more marked as the amount of paraffin oil is increased (expt. 104, Fig. 3).

4. **Films of Pentadecylic Acid (Fig. 4).**—The addition of 1.5 g. of the paraffin oil to 1 g. of pentadecylic acid increases the film pressure very greatly, both above and below the kink in the curve. However, at about 20 sq. Å. per molecule the two sets of curves cross. The curve for experiment 97 indicates that the tetradecane has evaporated.

5. **Surface Potentials of Polymolecular Films.**—Figure 5 exhibits interesting relations and shows that there is a kink in the potential area curves of both the pure acid and the mixture.

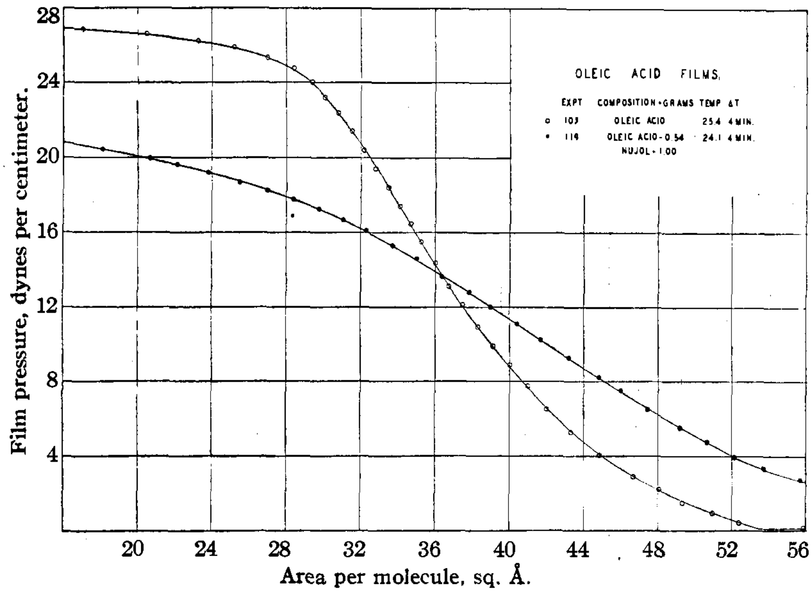

Fig. 2.—Poly- and mono-molecular films with oleic acid.

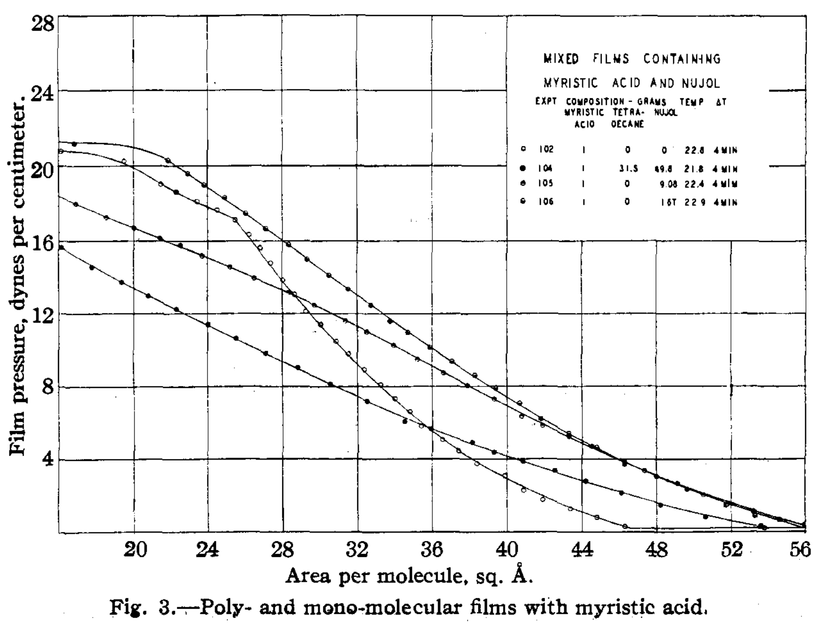

Fig. 3.—Poly- and mono-molecular films with myristic acid.

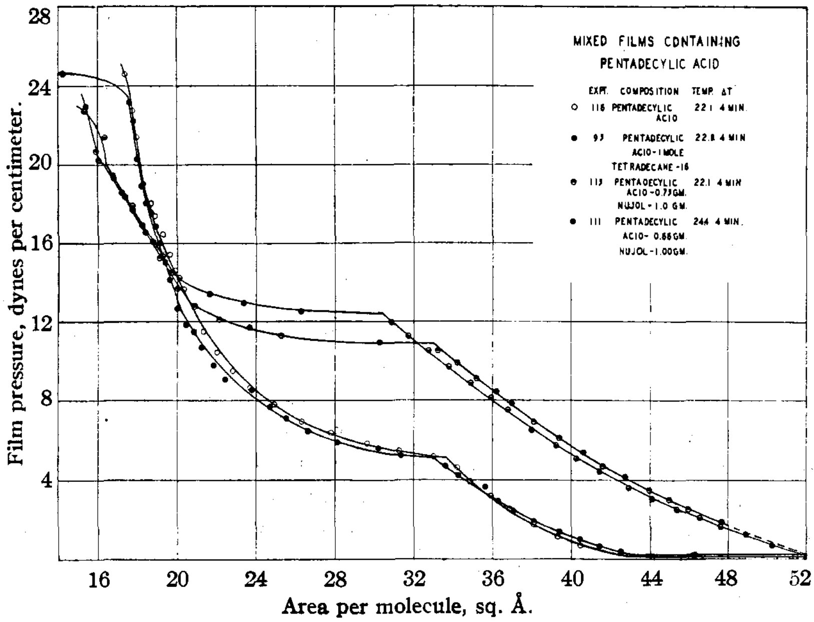

Fig. 4.—Poly- and mono-molecular films with pentadecylic acid.

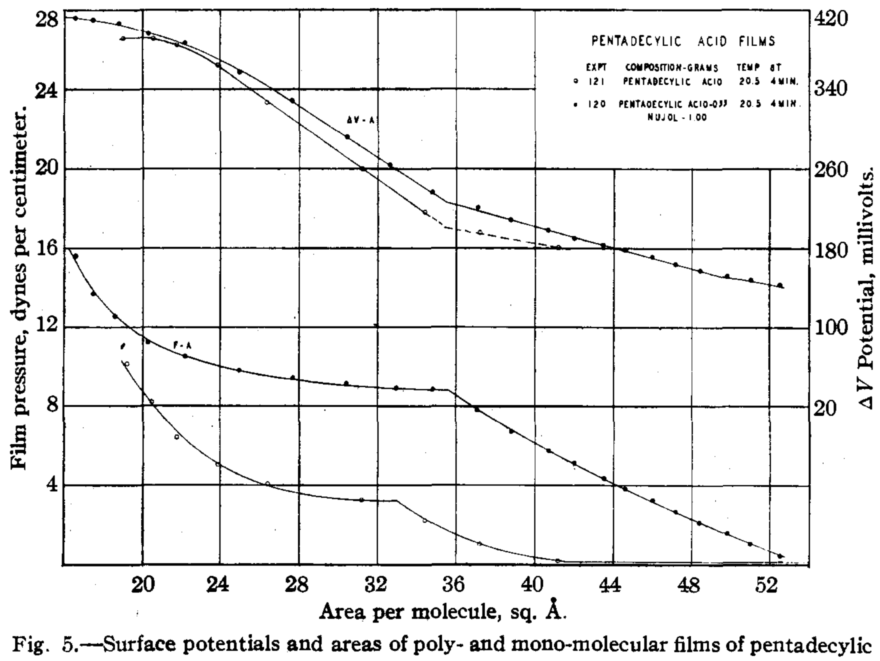

Fig. 5.—Surface potentials and areas of poly- and mono-molecular films of pentadecylic acid.

Polymolecular films exhibit many interesting relations, and many of these are under investigation in this Laboratory. At constant pressure many polymolecular, as well as monomolecular, films shrink with time. This shrinkage is very marked with pentadecylic acid at areas just below and pressures just above that of the kink in the curve.

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Micro Determination of Active Hydrogen with Deuterium Oxide

BY ROGER J. WILLIAMS

The usual methods of determining active hydrogen involving the use of a Grignard reagent, cannot be applied to highly water soluble materials which do not dissolve in ethers or other organic solvents.