

ortho, para ratio in the halogenation of aromatic compounds.

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#### OPTICAL MEASUREMENT OF THE THICKNESS OF A FILM ADSORBED FROM A SOLUTION

Sir:

A single layer of molecules deposited from a water surface on a built-up film produces [I. Langmuir, V. J. Schaefer and D. Wrinch, *Science*, **85**, 76-80 (1937); K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937)] a perceptible change in the color given by interference of light from the top and bottom of the film.

We can condition the surface of the built-up film to enable it to adsorb organic or inorganic substances from solution, and determine the dimensions of adsorbed molecules by the change in color.

Dipping the film into a solution containing a second substance reactive to the first, a second adsorbed film can be formed. Sometimes successive alternating layers can be built.

One method of conditioning a plate is to deposit upon it an A-layer of stearic acid from a water surface and to bring it into an aluminum chloride solution ( $10^{-3}$  molar). After washing, it is ready to adsorb many organic substances which contain polar groups.

For example a drop of a 1% solution of egg albumin is applied to the wet plate which is then washed and dried. The apparent increase in thickness is equivalent to 2 barium stearate layers (50 Å.). With Stanley's tobacco virus protein we obtain a maximum thickness of 12 stearate layers equivalent to 300 Å.

A surface conditioned by a monolayer of egg albumin deposited from a water surface takes up an adsorbed film of tobacco protein having a maximum thickness of only 5 stearate layers. This may be the thickness of molecules lying flat on the surface. Adsorbed films of other proteins on aluminized surfaces give films of from 2 to 8 stearate layers. As these are not always proportional to the cube root of the molecular weight, some protein molecules seem to be non-spherical.

It facilitates the formation of a complete layer to apply the protein in successive stages, washing

and drying the plate after each addition of the protein, probably because of consolidation by surface tension.

The molecular dimension (normal to the surface) of adsorbed molecules in a film which is only 70% complete may be determined by filling the interstices between molecules with hexadecane after covering with 4 barium stearate layers to render the surface non-wettable by oil.

Coöperating with Dr. Harry Sobotka we have conditioned a surface by deposition of a monolayer of cholesterol (18 Å.). This surface takes digitonin from aqueous solution giving an adsorbed film of 36 Å. Another layer of cholesterol can be deposited and a second adsorbed film of digitonin, etc. These multilayers give accurate measurement of molecular dimensions.

With Dr. E. F. Porter, we have adsorbed diphtheria toxin on a plate conditioned by aluminum chloride obtaining a monofilm of 36 Å. On dipping the plate into diphtheria antitoxin, there was an increase in thickness of 75 Å. Successive alternating layers of toxin-antitoxin can be built up indefinitely.

Not only the thickness but many other properties of adsorbed films can be measured such as contact angles with various liquids, solubilities, adsorbing power for substances in solution, refractive index, etc.

We believe the methods outlined are useful for detecting and identifying minute amounts of substances of biological interest and for studying the structure, reactivities and other properties of these substances.

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IRVING LANGMUIR  
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#### PHENOXYPYRIDINE

Sir:

Thanks to Professor Chichibabin, my attention has been called to some inaccuracies in a recent article by Renshaw and Conn [THIS JOURNAL, **59**, 297 (1937)], where the statement is made: "A number of 2-pyridyl ethers were prepared by heating 2-bromopyridine with the alkali salts of alcohols and phenols . . ." and farther on: "This is a more satisfactory method than that reported by Chichibabin [*J. Russ. Phys.-Chem. Soc.*, **50**, 502 (1918)] for the preparation of 2-phenoxy-pyridine, the only alpha-substituted pyridine reported in the literature."