

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

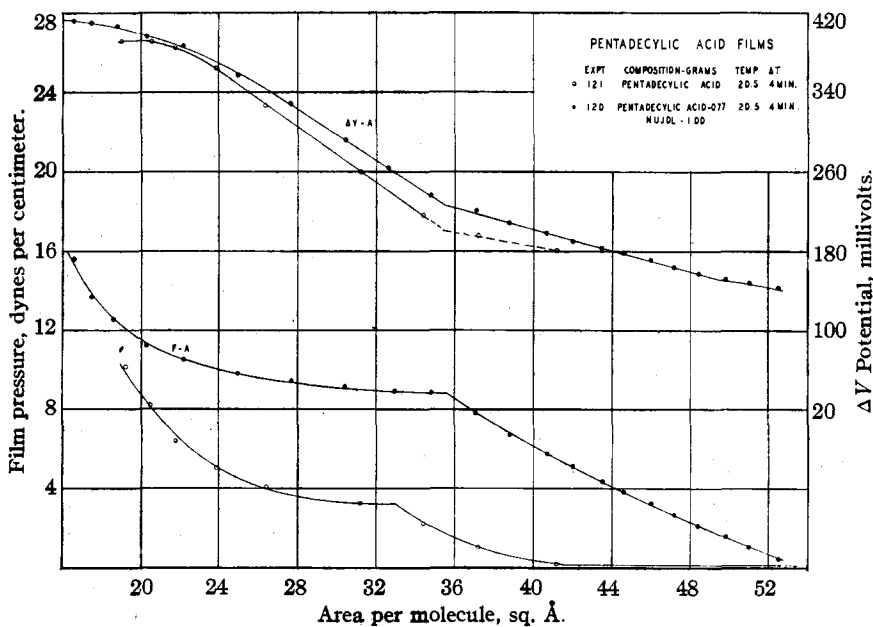


Fig. 5.—Surface potentials and areas of poly- and mono-molecular films of pentadecylic acid.

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.

We early suggested¹ the determination of active hydrogen by dissolving the unknown in deuterium oxide followed by a determination of the changed density of the water distilled off. Others^{2,3} have independently made use of the principle.

An experimentally simple embodiment of the same principle has now occurred to us which consists merely in dissolving the substance to be analyzed in deuterium oxide, evaporating to dryness and determining the increase in weight due to the replacement of active hydrogen by deuterium. This method has been applied to two known substances and the results are given in the following table. Other experimental work along similar lines which need not be detailed here has convinced us of the applicability of the method. The substances in small weighing bottles were simply dissolved in 0.25 ml. of 99.5% deuterium oxide and then carefully evaporated and dried to constant weight in vacuum desiccators, and weighed again.

Substance analyzed	Hydroxyproline			Urea		
	2H	3H	4H	3H	4H	5H
Sample, mg.						
After treatment, mg.						
Incr. after subtr. 5 γ blank						
Calcd. increases	0.128	0.192	0.256	0.297	0.383	0.479

The theoretical increases were calculated on the basis of complete replacement by deuterium. This assumption would introduce practically no error in the first determination and a very slight error in the second. A small increase in weight, about 5 γ , is noted when a glass weighing bottle itself is treated with heavy water.

The method need not be limited to water soluble substances since interchange should occur in ether or pyridine solution. In case of compounds which do not dry readily, appropriate means will have to be taken to bring the material to the same degree of dryness before and after treatment with deuterium oxide. Since the principle is so simple and the manipulation involves nothing beyond drying and weighing, it appears that no serious difficulty should be involved in applying the method. We hope other investigators to whom this type of work is less incidental, will perfect and extend the

(1) Roger J. Williams, "Introduction to Organic Chemistry," third edition, D. Van Nostrand Co., New York, 1935, p. 576.

(2) Bonhoeffer and Brown, *Z. physik. Chem.*, **223**, 172 (1933).

(3) Hamill and Freudenberg, *THIS JOURNAL*, **57**, 1427 (1935).

method which has been experimented with in our laboratory only in a preliminary way.

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Some Bismuth Derivatives of Diphenyl

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Since the number of known organic compounds of bismuth is meager, previous work on diphenyl derivatives of the arsenic group has been extended to include this element.¹ Arylation was accomplished through the organo magnesium compound, for the Wurtz-Fittig method employing sodium, used so successfully with other members of the group, failed with bismuth.

Experimental

Tri-biphenylbismuth.—One hundred grams of *p*-bromodiphenyl was changed into the magnesium compound according to the directions of Bent.² After dilution with several volumes of ether, 36 g. of powdered bismuth chloride was added directly (in small lots) with shaking and the mixture allowed to stand overnight. The ether was removed by decantation, after which the residue was decomposed as usual. A small amount of dilute acid was added to remove basic salts. The black precipitate was then filtered, dried and extracted successively with hot alcohol and chloroform. A small amount of dibiphenyl separated from the chloroform extract on cooling, after which the filtrate was concentrated to a small volume. On the addition of an equal volume of alcohol a crystalline product formed; yield approximately 43 g.

Anal. Calcd. for $C_{36}H_{27}Bi$: C, 64.7; H, 4.0. Found: C, 65.0; H, 4.3.

It is insoluble in alcohol, but dissolves readily in chloroform, separating in the form of tiny flat needles that melt at 182–183°.

Tri-biphenylbismuth Dichloride.—To the above substance dissolved in carbon tetrachloride was added chlorine dissolved in the same solvent; yield nearly quantitative. The product was recrystallized from chloroform-alcohol mixture, from which it separated as small plates melting with decomposition at 198–200°, if heated slowly.

Anal. Calcd. for $C_{36}H_{27}BiCl_2$: Cl, 9.6. Found: Cl, 9.5.

The dibromide prepared in a similar manner formed pale yellow plates that melted indefinitely with decomposition when heated.

Anal. Calcd. for $C_{36}H_{27}BrBr_2$: Br, 19.3. Found: Br, 19.1.

Both halides dissolved in fuming nitric acid, forming nitro derivatives that deflagrated if heated quickly.

Di-biphenylbismuth Chloride.—This was prepared by the method of Challenger³ using bismuth chloride with the

(1) Worrall, *THIS JOURNAL*, **52**, 664 and 2046 (1930).

(2) Bent, *THIS JOURNAL*, **54**, 1398 (1932).

(3) Challenger, *J. Chem. Soc.*, **107**, 19 (1915).