

TABLE III

## PHYSICAL PROPERTIES OF THE AMINE OXIDES

Compound	$\mu \times 10^{18}$	M. p., °C.	Mol. wt.	Sol., %
(CH <sub>3</sub> ) <sub>3</sub> NO	5.02	212	75	<0.03
(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> NO	4.79	154	137	0.8
C <sub>5</sub> H <sub>5</sub> NO	4.24	67	95	>1.2

The melting points of the series of related amine oxides show the increase expected in view of the increasing dipole moments. Although various factors such as molecular weight and hydrogen bond formation influence the melting points of compounds, it is apparent that in the amine oxides the relatively large permanent dipoles make dominant contributions to van der Waals forces. Contrary to the usual relationship for a series of closely related compounds, trimethylamine oxide with the lowest molecular weight has the highest melting point. The solubilities of trimethylamine oxide, dimethylaniline oxide and pyridine oxide in the non-polar solvent benzene increase rapidly in the order named. As this increase in solubilities parallels the decrease in melting points

and dipole moments of the amine oxides, these results corroborate the usual relationships<sup>22</sup> found for a series of like compounds.

## Summary

A heterodyne beat apparatus has been employed to measure the dipole moments of trimethylamine oxide, dimethylaniline oxide and pyridine oxide in benzene and in dioxane. The results support the electronic structures assigned to trimethylamine oxide and dimethylaniline oxide but it is concluded that pyridine oxide resonates among several structures. The relation of the dipole moments of the amine oxides to other physical properties is discussed.

The value 4.38 calculated for the dipole moment of the <sup>+</sup>N-O<sup>-</sup> link is larger than the moments of other semipolar bonds and an explanation of this difference is given.

(22) Cowley and Partington, *J. Chem. Soc.*, 1252 (1933); Hildebrand, *Science*, **83**, 21 (1936).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## A Study of Monolayers of Some Esters and Chlorinated Derivatives Possibly Useful as Lubricating Addition Agents

BY GEORGE L. CLARK AND JAMES V. ROBINSON<sup>a</sup>

### Introduction

The experimental work to be described furnishes evidence from which may be deduced the orientation in monomolecular films of certain substituted straight chain methyl esters upon a water surface. The interest in the problem was inspired by the need in the oil industry to know the mechanism of action of certain polar organic compounds, which, when added to a lubricating oil, increase its "oiliness." Of the various theories of this mechanism, the one considered in this investigation is that the addition agent is adsorbed on the metal, acting as a buffer between the metal surfaces. X-Ray diffraction has been used previously in this Laboratory to show that such an adsorption actually takes place.<sup>1,2</sup>

The monomolecular film balance was selected as a tool to furnish quantitative data on the strength

of adsorption, and the nature of the molecular packing of materials used as "oiliness" agents. It is suggested that the collapse-pressure of monomolecular films, measured on the hydrophil balance, may be correlated with the resistance to shear of the same substances oriented on a metal surface in an engine bearing. It is also suggested that a surface consisting of a close-packed array of hydrogen atoms, attached to hydrocarbon chains, should offer the minimum hindrance to the hydrocarbon molecules of a lubricating oil slipping over it.

The history and development of the hydrophil balance have been described recently in the literature.<sup>3,4</sup> The fundamental principles governing the interpretation of data from the hydrophil balance are the Principle of Short Range Forces, the Principle of Independent Surface Action, and stereochemical considerations.<sup>4</sup>

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(1) G. L. Clark, R. R. Sterrett, and B. H. Lincoln, *Ind. Eng. Chem.*, **28**, 1318-1328 (1936).

(2) G. L. Clark, R. R. Sterrett, and B. H. Lincoln, "The Science of Petroleum." Oxford University Press, 1936, p. 2566-2575.

(3) N. K. Adam, "Physics and Chemistry of Surfaces." Oxford at the Clarendon Press, second edition, 1938.

(4) I. Langmuir, *Proc. Roy. Soc. (London)*, **A170**, 1-39 (1939).

### Apparatus

The apparatus consists of the film balance<sup>5</sup> set in a large air thermostat, with controls permitting manipulation of the barrier determining the area, and the torsion head measuring the pressure, from outside of the case. The toluene-expansion thermoregulator is immersed in the water of the trough, maintaining the temperature of the water constant within one-half degree. A detailed technique for making the determinations was worked out.

### Experimental Results

The series of compounds studied was the methyl esters of certain substituted, eighteen carbon, straight chain fatty acids. The compounds are: methyl stearate, ethylene glycol distearate, methyl oleate, methyl ricinoleate, methyl 9,10-dichloro-12-hydroxystearate (chlorinated methyl ricinoleate), and ethylene glycol ricinoleate. Tricresyl phosphate is reported incidentally. These were either carefully synthesized or obtained from reliable sources and re-purified. Analysis of the chlorinated derivatives did not always indicate exactly stoichiometric ratios, but were typical of all such esters.

With the apparatus it is possible to make measurements with high precision, but it is found that the monomolecular films have a greater or lesser degree of reproducibility which is characteristic of the substance in the film.<sup>6</sup> The variations in results may therefore be very large or very small, dependent upon the compound.

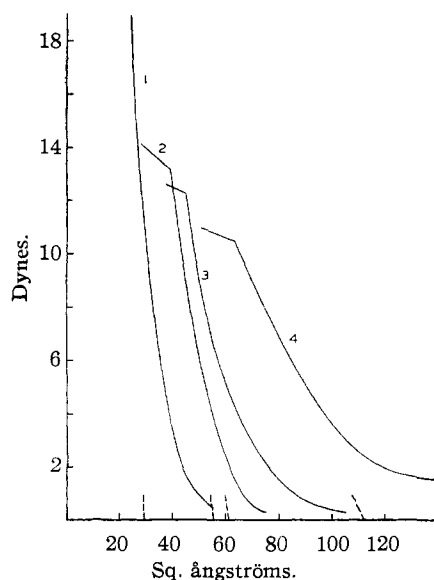


Fig. 1.—Film balance measurements for monolayers on a water surface of molecular areas in square ångströms as functions of pressures in dynes per cm.: 1, methyl stearate; 2, methyl  $\alpha$ -chlorostearate; 3, methyl dichlorostearate; 4, tricresyl phosphate.

The experimental results are summarized in Tables I and II, respectively, for films on pure water and on chlorine water (0.02  $M$ ). Curves for area per molecule as a func-

(5) Technical Bulletin 102, Central Scientific Co., Chicago.

(6) W. D. Harkins and G. C. Nutting, *THIS JOURNAL*, **61**, 1180 (1939).

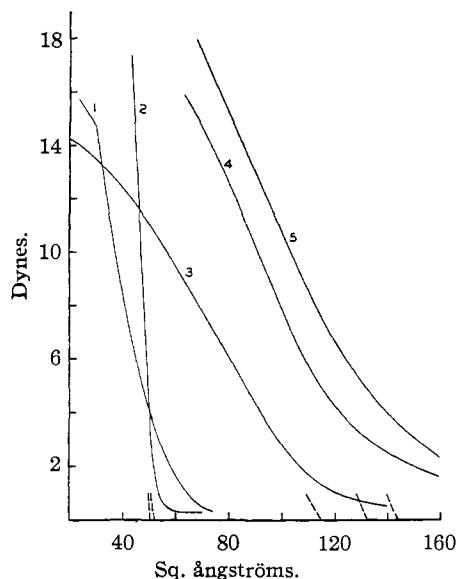


Fig. 2.—Film balance measurements for monolayers on a water surface of molecular areas in square ångströms as functions of pressures in dynes per cm.: 1, methyl oleate; 2, ethylene glycol distearate; 3, chlorinated methyl ricinoleate; 4, methyl ricinoleate, 25°; 5, methyl ricinoleate, 30°.

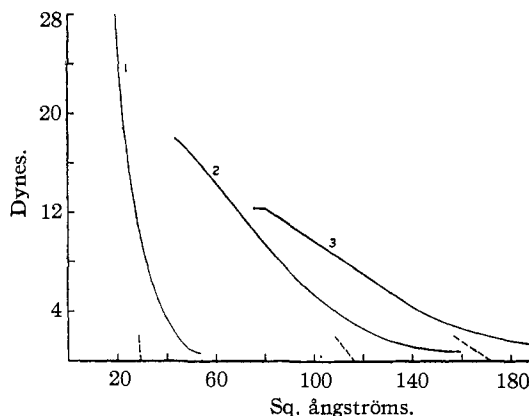


Fig. 3.—Film balance measurements for monolayers on a chlorine water (0.02  $M$  in  $Cl_2$ ) surface of molecular areas in square ångströms as functions of pressures in dynes per cm.: 1, methyl stearate; 2, methyl oleate; 3, methyl ricinoleate.

tion of pressure on the monolayer in dynes per sq. cm. are presented in Figs. 1, 2 and 3. Extrapolation for zero compression gives the values for the areas per molecule listed in Tables I and II.

### Discussion of Results

The area per molecule assumed by methyl stearate on the water surface is nearly doubled by the presence of one chlorine atom in the chain (methyl  $\alpha$ -chlorostearate) and further increased by the presence of two chlorine atoms (methyl di-

TABLE I  
 FILMS ON PURE WATER

	Temp., °C.	Num- ber dets.	Area at zero compression		Collapse pressure, dynes per cm.
			Sq. Å.	Av. dev. from av., %	
Methyl stearate	30	7	30.4	4.08	20
	25	2	26.3	0.96	
Methyl $\alpha$ - chlorostearate	30	8	55.1	3.30	13
	25	2	53.3	6.11	
Methyl dichlo- rostearate	30	3	62.7	5.05	12.5
	25	4	59.8	1.96	
Methyl oleate	25	3	52.0	3.50	14.5
Ethylene glycol distearate	30	6	49.5	2.52	19
	25	1	51.0		
Methyl ricinoleate	30	11	147.8	2.90	19
Chlorinated methyl ricinoleate	25	3	131.6	0.19	10. (?)
	30	5	113.7	0.38	
Ethylene glycol ricinoleate	25	2	113.0	0.44	16.5
	30	5	253.0	4.23	
Tricresyl phosphate	30	5	111.8	2.55	10.5
	25	2	111.0	0.0	

 TABLE II  
 FILMS ON CHLORINE WATER

Substance	Temp., °C.	Time before compression, minutes	Area at zero compression	Collapse pressure
Methyl stearate	25	10	29.0	36
	25	3	29.0	
	25	3	29.5	
Methyl oleate	25	10	104	19
	25	15	109	
	25	20	118	
	25	10	145	
Methyl ricinoleate	25	10	145	12.5
	25	15	154	
	25	20	171	

chorostearate). The stability of the films of the chlorinated esters is less than that of methyl stearate. Calculations show that the increased area may be accounted for approximately by the bulk of the chlorine atoms. Other factors, such as polymerization catalyzed by metal surfaces, must account for the known effectiveness of methyl dichlorostearate as a lubricating addition agent in amounts less than 1%.<sup>1,2</sup>

The *cis* configuration of the olefinic linkage in methyl oleate prevents the molecules from packing into a condensed film of the methyl stearate type.<sup>7</sup>

The hydrophilic character of those compounds containing hydroxyl groups can be explained satisfactorily by the assumption that inter- or intramolecular hydrogen bonding between two hydroxyl groups decreases their hydrophilic charac-

ter as compared with a hydroxyl group in contact with the water only.<sup>7,8</sup>

With methyl ricinoleate, intermolecular hydrogen bridge formation is prevented by the *cis* configuration, hence the molecule is strongly hydrophilic at two points along its length. Hydrogen bonding evidently occurs between adjacent hydroxyl groups in chlorinated methyl ricinoleate, as indicated by the decrease in hydrophilic character from methyl ricinoleate.

The addition of hypochlorous acid to the double bonds of methyl oleate and methyl ricinoleate was studied by spreading these compounds upon an aqueous solution of chlorine in the film balance trough.

Methyl 9-chloro-10-hydroxystearate, formed by the addition of hypochlorous acid to a monomolecular film of methyl oleate, gives the same type of pressure-area curve as found for methyl ricinoleate. Apparently, addition of the hydroxyl group at the surface prevents it from forming other hydrogen bonds. Methyl 9-chloro-10,12-dihydroxystearate formed by the addition of hypochlorous acid to a monomolecular film of methyl ricinoleate, has the same type of curve as chlorinated methyl ricinoleate. This is interpreted as due to intramolecular hydrogen bonding between the two hydroxyl groups.

Ethylene glycol ricinoleate and ethylene glycol distearate have the same shape of curves and approximately twice the area per molecule as their respective methyl esters.

Tricresyl phosphate is less hydrophilic than the other compounds studied, and is apparently held to the water surface only by the unsaturated oxygen atom. This is indicated by the observation that triphenyl phosphite is as hydrophobic as a hydrocarbon.

**Built-up Films.**—The built-up film technique, originated by Blodgett,<sup>9</sup> was used in an attempt to correlate the arrangement of molecules on a water surface and a metal surface, and in the solid crystalline structure. The importance of such a correlation is to permit the use of the film balance data to predict the molecular arrangement preferentially assumed on a metal surface.

To the film balance was added a mechanical device for dipping solid slides through the water surface.<sup>10</sup> The film balance proper was not modi-

(8) E. K. Rideal and A. H. Hughes, *Proc. Roy. Soc. (London)*, **A140**, 253-269 (1933).

(9) K. B. Blodgett, *THIS JOURNAL*, **57**, 1007-1022 (1935).

(7) E. K. Rideal and J. Marsden, *J. Chem. Soc.*, 1163-1171 (1938).

(10) S. J. Gregg and E. E. Widdowson, *Rev. Sci. Instruments*, **10**, 236 (1939).

fied in any way. The barrier of the film balance was advanced to maintain any desired pressure on the monomolecular film during the dipping of the slide. This mechanical technique replaces the conventional "piston oil" and flexible barrier technique.

The effects of the nature of the backing material, the compression of the monomolecular film, the rate of dipping and the temperature upon the ability of the films to be picked up were studied. Certain generalizations may be made in regard to preparing built-up films. (1) The monomolecular films on the water surface must be in the "solid condensed" state to be capable of transferring many layers to a solid backing. (2) The formation of the "solid condensed" state is favored by increase in lateral pressure and decrease in temperature. (3) The condition of the backing surface is most important. A hydrophobic surface favors film deposition. (4) The highest speed of dipping that will not excessively agitate the surface is the most desirable. For this reason thin slides are preferred to thick ones.

Of the compounds in the series, only methyl stearate and ethylene glycol distearate formed built-up films more than two to five molecular layers thick. Even at a temperature of 10°, the other compounds formed "liquid" films from which only 2 to 5 monolayers could be picked up.

Electron diffraction studies of these films will be reported in a later paper.

The X-ray examination of the methyl stearate and ethylene glycol distearate confirmed the spacings found by others.<sup>11</sup>

### Summary

With an improved film balance under carefully controlled conditions measurements are made of area per molecule, and collapse pressure on water surfaces for monolayers of certain esters which have possible use as addition agents in lubricating oils, namely, methyl stearate,  $\alpha$ -chlorostearate, dichlorostearate, oleate, ricinoleate and chlororicinoleate, ethylene glycol distearate and ricinoleate, and tricresyl phosphate.

The addition of hypochlorous acid to the double bonds of methyl oleate and ricinoleate was studied by spreading monolayers on an aqueous solution of chlorine in the film balance trough.

Films are built up by the Blodgett-Langmuir technique. Only methyl stearate and ethylene glycol distearate formed solid condensed films which could be picked up in any number of monolayers and subjected to X-ray diffraction analysis. The remaining esters formed "liquid" films from which only 2 to 5 monolayers could be picked up for electron diffraction analysis.

(11) E. Stenhagen, *Trans. Faraday Soc.*, **34**, 1328-1337 (1938).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE INSTITUTUM DIVI THOMAE]

## Some Dialkylaminoalkyl Furoates and Benzoates as Topical Anesthetics<sup>1</sup>

BY ELTON S. COOK AND CORNELIUS W. KREKE

Experience has shown that the acid portion of the aminoester local anesthetic molecule is, in general, preferably aromatic.<sup>2</sup> Interest therefore attaches to a comparison of the ability of various aromatic groups to confer local anesthetic activity. The early paper of Gilman,<sup>3</sup> dealing with the  $\beta$ -diethylaminoethyl esters of acids containing aminobenzene, benzene, pyrrole, thiophene and furan rings, showed all of the esters to possess low topical activity. The intracutaneous activity decreased in the order given, the furan compound

barely showing activity even by this method of testing. Phatak<sup>4</sup> confirmed this fact but found that the substitution of alkyl groups in the 5-position of the furan ring brought about topical activity. Phatak and Emerson<sup>5</sup> earlier found that simple alkyl esters of 2-furoic acid possessed activity whereas the corresponding benzoates were inactive; ethyl esters of 5-alkyl-2-furoic acids, however, were inactive.<sup>4</sup> Walter<sup>6</sup> reported that, while the difuroate of 1-piperidinopropane-2,3-diol was less active than the corresponding diben-

(1) Presented before the Division of Medicinal Chemistry, Cincinnati meeting of the American Chemical Society, April 11, 1940.

(2) For discussion see E. S. Cook, *Studies Inst. Divi Thomae*, **2**, 63 (1938).

(3) H. Gilman and R. M. Pickens, *THIS JOURNAL*, **47**, 245 (1925).

(4) N. M. Phatak, *Univ. Calif. Pub. Pharmacol.*, **1**, 55 (1938).

(5) N. M. Phatak and G. A. Emerson, *J. Pharmacol.*, **58**, 174 (1936).

(6) E. M. Walter, *THIS JOURNAL*, **60**, 2467 (1938).