

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Flow of Unimolecular Surface Films

BY E. ROGER WASHBURN AND HELMUT RICHARD R. WAKEHAM

The viscosity of unimolecular films has been described recently by W. D. Harkins and R. J. Myers.¹

These workers have recorded the viscosity of stearic acid films on water at 25° as 0.000307 dyne sec. cm.⁻¹. The authors of this report also have been studying the flow of monomolecular films of stearic acid on water. Our interest has been in the effect of the various factors which influence the rate of flow. Among these factors are temperature, pressure, and hydrogen ion concentration of the water on which the film is floated.

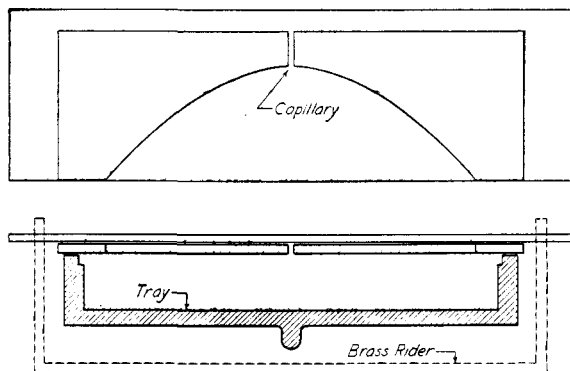


Fig. 1.

Materials

Stearic Acid.—Eastman quality stearic acid was used. It had a melting point (corrected) of 68.9°. The "International Critical Tables" list 69.3°.²

Benzene.—Mallinckrodt reagent grade benzene was used as a solvent for the parawax and parawax-beeswax mixture which was applied to the tray and barriers. This was sometimes used as a solvent for the stearic acid and sometimes it was mixed with a good grade of petroleum ether for that purpose. Neither the benzene or the ether contained material which formed troublesome surface films.

Water.—Redistilled water was buffered with the citric acid- Na_2HPO_4 mixtures as described by McIlvaine³ in order to have a medium of constant and reproducible hydrogen ion concentration on which to float the film. The hydrogen ion concentration was measured from time to time with a "Wulff" colorimetric pH tester. This outfit was in turn compared with carefully prepared standard buffer solutions. Because of the effect that buffer salts

have on the area of surface films and because of the decreased need for high concentrations since the work was carried out in a closed cabinet, less than the recommended concentrations were usually used.

Apparatus and Procedure

A commercial modification of the Langmuir apparatus known as the "Cenco Hydrophil Balance" was the chief piece of equipment. This was set up in a small glass sided wooden cabinet. A glass barrier with a parabola shaped opening leading to the capillary was mounted in a brass rider as shown in Fig. 1. The internal width of the tray was 14.0 cm. The capillary used in obtaining the results given in this report was 1.38 cm. long and 0.111 cm. wide.

The brass rider with its glass barrier and small opening was pulled toward the mica float attached to the torsion head, by a system of pulleys, belts and cords and a variable speed motor mounted outside of the cabinet. The film pressure was obtained from the reading on the torsion head while the pointer was kept on the reference mark as the film flowed through the opening. The torsion head had been calibrated previously by the usual method of hanging weights on the arm attached to the steel wire which was then twisted until the pointer moved to the reference mark. An extension arm permitted the torsion head to be operated from the outside of the closed cabinet. Readings were taken from time to time and the speed of the motor was controlled as necessary to keep the pointer on the mark.

It hardly should be necessary to point out that the utmost cleanliness of everything within the cabinet was necessary in order even to approach reproducible results. Care also had to be exercised to see that the drops of the benzene solution of the stearic acid did not spread out so as to touch the paraffined sides of the tray or a very troublesome film of paraffin was formed.

Results

The following data are typical of those obtained with stearic acid films. The solutions were buffered with one third of the standard concentrations of McIlvaine's buffers.

Each of the film pressures listed is a calculated value obtained from the dial reading for the particular run and the calibration of the steel wire. Each of the values listed under rate of flow is an average rate obtained while 250 to 300 sq. cm. of film was caused to flow through the capillary for a fixed setting of the dial. The value for the rate in molecules per second was obtained in each case by dividing the area per second by the area per molecule as determined from a film pressure-area curve obtained under the same conditions as

(1) Harkins and Myers, *Nature*, **140**, 465 (1937); *J. Chem. Phys.*, **5**, 801 (1937). See also Harkins and Kirkwood, *ibid.*, **6**, 53 (1938).

(2) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. I, p. 264.

(3) McIlvaine, *J. Biol. Chem.*, **49**, 183 (1921).

TABLE I

ρH , 7.0; temperature, 27°			
Film pressure, dynes/cm.	Rate of flow, cm. ² /sec.	Molecules/sec.	Viscosity
3.1	0.448	17.8×10^{13}	0.000556
4.5	.686	27.6×10^{13}	.000542
7.7	.994	41.0×10^{13}	.000641
9.2	1.232	51.0×10^{13}	.000618
12.3	1.344	57.4×10^{13}	.000758
15.4	1.666	72.9×10^{13}	.000764
18.4	2.030	90.4×10^{13}	.000750
21.5	1.946	88.5×10^{13}	.000914
24.6	2.002	93.2×10^{13}	.001023
27.7	2.030	96.3×10^{13}	.001130
33.8	2.296	110.0×10^{13}	.001217
40.0	2.506	120.4×10^{13}	.001321
43.0	2.646	127.8×10^{13}	.001343
49.2	2.982	144.5×10^{13}	.001367
55.3	3.262	159.2×10^{13}	.001402
61.4	3.780		.001321
63.0	4.116		.001267
64.5	6.370		.000460
67.6	19.880		.000281

These results are plotted in Fig. 2.

those maintained for the above table. The numbers under the caption "viscosity" are the figures which result when values from our experiments were substituted in the equation proposed by Harkins and Myers.¹

Discussion

These experiments seem to indicate that the area of film which flows through the capillary employed increased with the film pressure applied but not in a straight line relationship throughout a great change in pressure. Since increased pressure on a film alters the area occupied by each molecule as well as the rate of flow of the film, it would seem that such a curve as that shown in Fig. 2 (A) in which rate is expressed in molecules per second might be more significant than when area per second is used.

For like pressures, films on acid solutions flow more rapidly than films on neutral solutions. The two main forces retarding the motion of the film through the capillary opening may be considered as intermolecular friction between the oriented acid molecules and the friction between the acid molecules and the water. The first may be due to the lateral cohesion between

TABLE II

SAME CONDITIONS AS FOR TABLE I EXCEPT THAT $\rho\text{H} = 3.8$			
Film pressure, dynes/cm.	Rate of flow, cm. ² /sec.	Film pressure, dynes/cm.	Rate of flow, cm. ² /sec.
3.1	0.616	18.4	2.380
4.5	.980	21.5	2.646
6.1	1.176	24.6	2.800
7.7	1.470	27.7	2.912
9.2	1.526	30.7	3.780
12.3	1.848	36.9	5.600
15.4	2.128		

These results are plotted in Fig. 2.

TABLE III

ρH , 7.0			
Film pressure, 4.6 dynes/cm.	Temp., °C.	Film pressure, 7.7 dynes/cm.	Temp., °C.
Rate in cm. ² /sec.		Rate in cm. ² /sec.	
22.6	0.588	21.6	1.092
26.0	.700	22.5	1.092
26.8	.686	23.3	1.162
29.5	.826	24.5	1.176
29.7	.826	25.6	1.288
30.0	.854	26.7	1.302
30.3	.882	28.6	1.428

These results are plotted in Fig. 3.

the oriented hydrocarbon chains of the acid molecules. The second retarding force may be due to

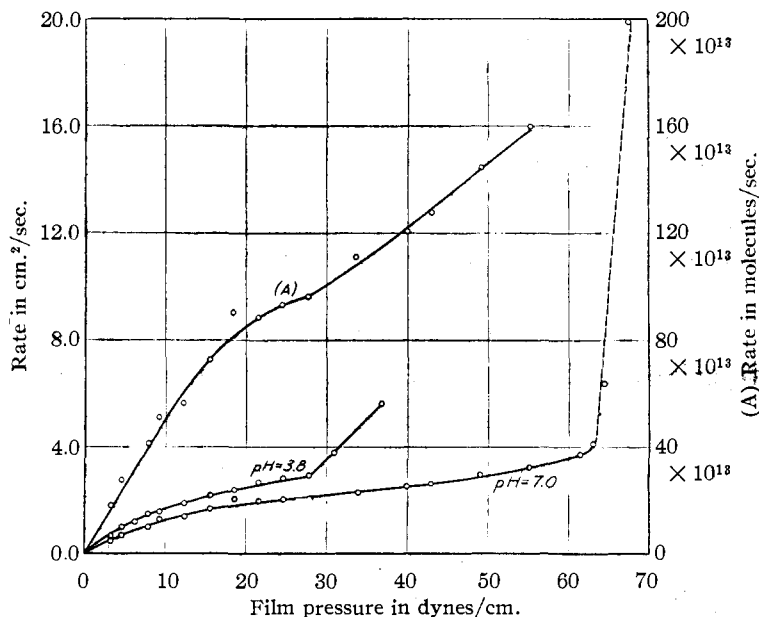


Fig. 2.

the adhesion between the carboxyl groups of the acid molecules and the water. This second force will of necessity vary with the acidity of the substrate water and will be less the greater the acidity. It would be expected that the friction between the acid molecules and the water would be less on the

acid solution and hence the rate of flow would be greater.

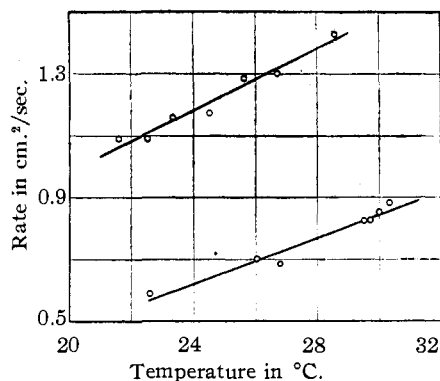


Fig. 3.

A study of film pressure-area relationships for stearic acid films under conditions identical with those for Tables I and II indicates that the transition from liquid to solid film takes place at about 27 dynes/cm. for both pH 7.0 and 3.8. The collapse of the film on the more acid solution occurred at a lower pressure, about 40 dynes/cm., than on the neutral solution, about 60 dynes/cm. The nearly vertical portions of the rate-pressure curves indicate that collapse of the film has taken place. In other words at the pressures at which the curve is nearly vertical the film crumples instead of flowing through the capillary. The results plotted in Fig. 2 indicate that the solid film flows through the opening more rapidly than the liquid film. This rather surprising observation may not seem so peculiar when one remembers that the

film pressures on the solid film are greater than on the liquid film and that the rate of flow is determined not only by intermolecular friction between the like molecules in the film but also by friction between the film and the liquid on which it flows. While we would expect the friction between molecules of a solid film to be greater than that between molecules of a liquid film, the friction between the solid film and water should not be much different from that between the liquid film and water. Investigation of Fig. 2 and Table I indicates that the rate of flow of the solid film does not increase as rapidly, with increase in film pressure, as does the rate of flow of the liquid film. A consideration of the calculated values of viscosity shows that the solid film has a greater viscosity than the liquid film and that the viscosity of the solid film varies less with pressure than does the viscosity of the liquid film.

Our experiments indicate that for like pressures and hydrogen ion concentration films flow more rapidly at higher temperatures than at lower temperatures. Further the temperature coefficient seems to be greater at a low pressure than at a higher pressure.

Summary

The rate of flow of unimolecular surface films of stearic acid on water has been studied.

Observations have been made regarding the effect of film pressure, temperature, and hydrogen ion concentration of the substrate water, on the rate of flow.

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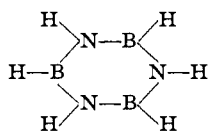
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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. IX. The Preparation of Some Methyl Triborane Triamines

BY H. I. SCHLESINGER, DAVID M. RITTER¹ AND ANTON B. BURG

Triborane triamine ($B_3N_3H_6$)² was first prepared by Stock and Pohland,³ who assigned to it the ring structure shown, on the basis of the evidence available at the time. The electron diffraction work of Stock and Wierl⁴ substantiated the ring



structure shown, on the basis of the evidence available at the time. The electron diffraction

structure. It was considered desirable, however, to test this structure further by a study of the methyl derivatives of the compound.

The preparation of derivatives in which methyl groups are attached to boron atoms of the ring, has been described by Schlesinger, Horvitz and Burg,² who found it possible to prepare three and only three such derivatives (by reactions of the methyl diboranes with ammonia), a result in agreement with the structure proposed by Stock and Pohland. The present work includes a parallel set of results: three and only three derivatives in which methyl groups are attached to the ni-

(1) This paper is taken from a dissertation presented by David M. Ritter to the Faculty of the Division of Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) This compound was not named at the time of its discovery. The name used here was suggested by Schlesinger, Horvitz and Burg, THIS JOURNAL, **58**, 409 (1936).

(3) Stock and Pohland, *Ber.*, **59B**, 2215 (1926).

(4) Stock and Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).