We are grateful to Dr. R. F. Nickerson for the use of some data obtained in preliminary experiments.

Summary

Cottonseed meats have been ground and extracted with ether. The effect of pH and of a number of salts on the extraction of the nitrogenous constituents from the meal is recorded.

PITTSBURGH, PENNA. RECEIVED MAY 22, 1939

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

The Pressure–Area and Pressure–Temperature Relations of Expanded Monolayers of Myristic and Pentadecylic Acids

BY GEORGE C. NUTTING AND WILLIAM D. HARKINS

1. Introduction

At 25° when spread on water which contains 0.01 N hydrogen ion, margaric ($C_{16}H_{33}COOH$) and higher saturated fatty acids form films which condense rather abruptly at pressures of about 0.5 dyne per cm. to slightly viscous, slightly compressible liquids whose area per molecule extrapolated to zero pressure varies only from about 23 to 24.5 sq. Å.

Lower members, specifically myristic and pentadecylic acids, exhibit a widely different behavior on compression. The limiting area at zero pressure is 46 sq. Å. per molecule. The compressibility is high and the pressure–area plots instead of being linear have a marked concave curvature upward. At a pressure characteristic of the particular acid a break occurs in the pressure–area curve such that the decrement of area per unit increase in pressure increases greatly; that is, the compressibility becomes very high. The curve above the break passes finally into a form characteristic of condensed films. A film which acts in this way is designated below the kink as an expanded film, and above it, until the area per molecule is about 23 sq. Å., as a transition or intermediate film.

The higher fatty acids give similar expanded and intermediate films at higher temperatures. The existence of the expanded state was recognized and investigated by Labrouste[1] and films of this type have been investigated in great detail by Adam and others.[2]

2. Apparatus and Materials

Pressure–area measurements were made with a film balance closely similar to one described by Harkins and Myers.[3] Subsolutions were contained in a shallow trough of stainless steel equipped with a false bottom through which water from a large reservoir was circulated. The trough and film balance were contained in a metal box with a front of plate glass. The top of this box was hollow, and water from the same thermostat was circulated through it in order to keep the temperature the same as that of the trough. This box was surrounded by an air thermostat kept as closely as possible at the temperature of the inner box. Thermocouples were installed just above and just below the film and when the air and the subsolution temperatures were equal it was assumed that the film also was at the same temperature.

In all of the experiments the films were spread on 0.01 N sulfuric acid prepared from water redistilled from alkaline permanganate and condensed in tin.

The myristic and pentadecylic acids were generously provided by Professor E. E. Reid of the Johns Hopkins University. The preparation and purification of the acids has been described by Reid and Meyer.[4] The acids were dissolved in purified ligroin (b. p. 60–70°) and spread from a precision pipet devised by Harkins and Anderson.[5] After spreading, a period of from fifteen to forty-five minutes was allowed before compression, during which it was assumed that any micro-crystals present would spread into a monolayer.

3. Pressure–Area Measurements

The pressure–area relations of myristic acid at seven temperatures from 6.7 to 25° are exhibited in Fig. 1 and Table I. So far as is possible, all experimental points are included, except that in the area interval 26–33 sq. Å. of Curve 4 and in a few other places, one-half the points have been omitted in order to avoid too great crowding. The time interval between adjacent points was never less than one minute, and except at the highest temperatures was commonly two to five minutes in the intermediate region. Area decrements also were not uniform but their magnitude may be judged from the curves.

It will be shown later that the rate of compression has a marked influence upon the pressure of

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[1] Labrouste, *Ann. Phys.*, **14**, 164 (1920).

[2] N. K. Adam, "The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, England, 1938.

[3] W. D. Harkins and R. J. Myers, *J. Chem. Phys.*, **4**, 716 (1936); G. C. Nutting and W. D. Harkins, THIS JOURNAL, **61**, 1180 (1939).

[4] E. E. Reid and J. D. Meyer, *ibid.*, **55**, 1574 (1933).

[5] W. D. Harkins and T. F. Anderson, *ibid.*, **59**, 2189 (1937).

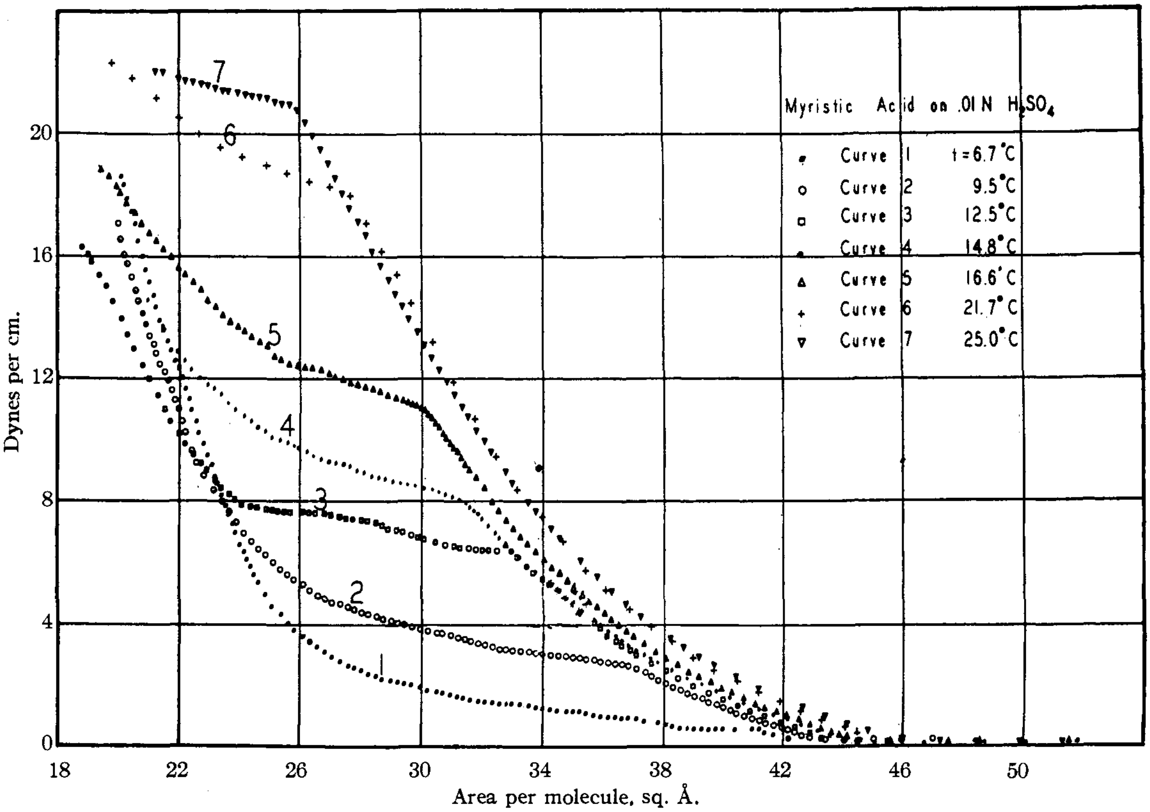

Fig. 1.—Pressure–area relations of myristic acid films. Curve 7 taken at 25° is displaced toward lower pressures and lower areas, especially at the highest temperatures, by the solubility of the myristic acid.

TABLE I

FILMS OF MYRISTIC ACID ON 0.01 *N* SULFURIC ACID

Temp., °C.	Time interval between points, sec.	Area decrements, sq. Å. per mol.	Limiting area, sq. Å. per mol.	Area at kink, sq. Å. per mol.	Press. at kink, dynes per cm.	Total time of expt., min.
6.7	..	...	43.0	41.2	0.58	236
9.5	..	...	44.5	36.9	2.65	293
12.5	..	...	44.5	32.8	6.18	171
14.8	..	...	45.2	31.5	7.95	253
16.7	..	...	45.1	(30.0)	(11.12)	159
	30	0.6	45.4	30.4	10.4	22
	15	1.2	46.5	31.4	10.0	6
21.7	60	0.7	46.9	27.6	18.1	39
25.0	60	0.3	46.4	25.9	20.9	77
	15	1.0	47.0	26.9	21.4	7.5

the intermediate film at any given temperature and molecular area. In the work of Adam and Jessop[6] the rate seems to have been much higher than that used in the present work. In the two investigations the pressures found for the transition Expanded → Intermediate film, are in good agreement, but our molecular areas for the transitions are about 10% lower than theirs. The total time (*t*) of a compression from the highest to the lowest area varied in our work from 39 minutes at 21.7° to 293 minutes at 9.5°.

The shape of Curve 7 in Fig. 1 is distorted by a spurious effect which causes it to be displaced toward lower areas, and decreases the pressure at the highest pressures. This is due to the solubility of the myristic acid which at 25° removes a part of the material from the film. Since the solubility increases with increase of film pressure as well as temperature the slope of the curve in the intermediate region is much too small.

4. The Rate of Compression

In order to determine the effect of the rate of compression on the form and position of pressure–area curves of expanded and intermediate films a series of experiments was carried out with both pentadecylic and myristic acids at several temperatures. The results are shown in Figs. 2, 3, 4, and 5, and in Tables I and II.

Comparing first the two acids, there is remarkable similarity between the curves for pentadecylic and those for myristic acid at a temperature

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[6] N. K. Adam and G. Jessop, *Proc. Roy. Soc.* (London), **A112**, 364 (1926).

TABLE II

FILMS OF PENTADECYLIC ACID ON 0.01 *N* SULFURIC ACID

Temp., °C.	Time interval between points, sec.	Area decrements, sq. Å. per mol.	Limiting area, sq. Å. per mol.	Area at kink, sq. Å. per mol.	Press. at kink, dynes per cm.	Total time of expt., min.
17.9	30	0.25	43.5	41.8	0.5	44
	15	.53	43.8	41.4	.6	11
	15	1.05	43.6	40.8	.7	5.5
21.7	30	0.25	44.6	35.6	4.6	44
	15	.54	45.5	36.4	4.3	12
	15	1.05	45.1	36.1	4.1	5.5
25.0	60	0.3	45.6	33.4	8.4	79
	15	.53	45.9	33.0	8.5	14
	15	1.05	46.1	32.8	8.3	7

11° lower. The principal difference is in the extent of minor irregularities in the intermediate region.

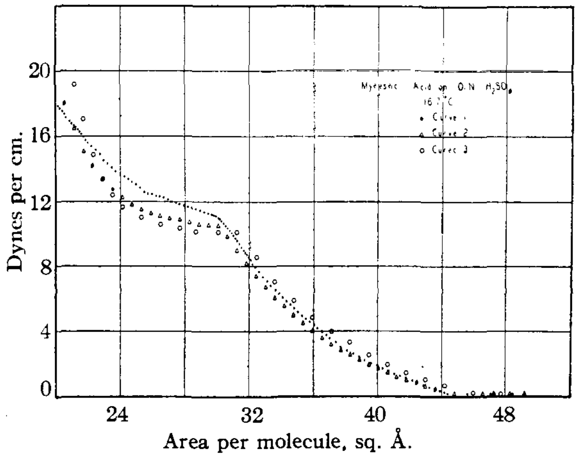

Fig. 2.—Effect of rate of compression on pressure-area relations of myristic acid films. Time of compression from limiting area at zero pressure to 20 dynes per cm.: Curve 1, 159 min.; Curve 2, 22 min.; Curve 3, 6 min.

The general rule is that a decrease in the rate of compression of an intermediate film causes: (1) an increase of molecular area at a given pressure; or (2) an increase of pressure at a given molecular area.

In Fig. 3 this effect is masked in the case of myristic acid by its relatively high solubility at 25° (Curves 1 and 2).

Results in reasonable accord with those reported in this paper for rapid compression have been obtained for myristic acid on 0.002 *N* hydrochloric acid by Dervichian,[7] who used the Wilhelmy method for measuring film pressures. The film was compressed at a very high, constant rate by a motor drive so that the total time of an experiment amounted to only about two or three minutes.

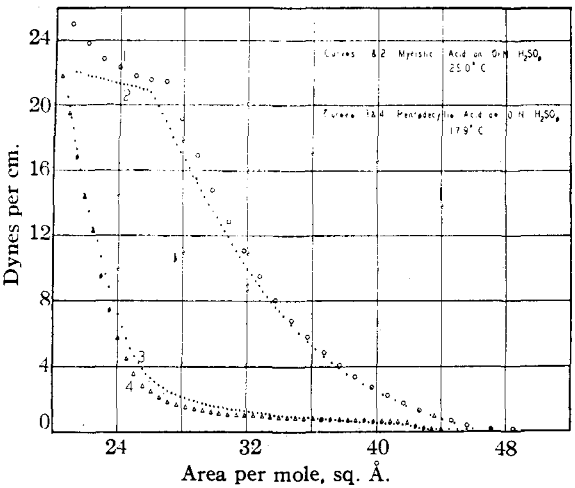

Fig. 3.—Effect of rate of compression on pressure-area relations of myristic and pentadecylic acids. Time of compression: Curve 1, 7.5 min.; Curve 2, 77 min.; Curve 3, 44 min.; Curve 4, 11 min. Curve 2 is depressed below Curve 1 by the solubility of myristic acid at 25°, so these two curves do not give the proper relations due to the effect of time on the film itself.

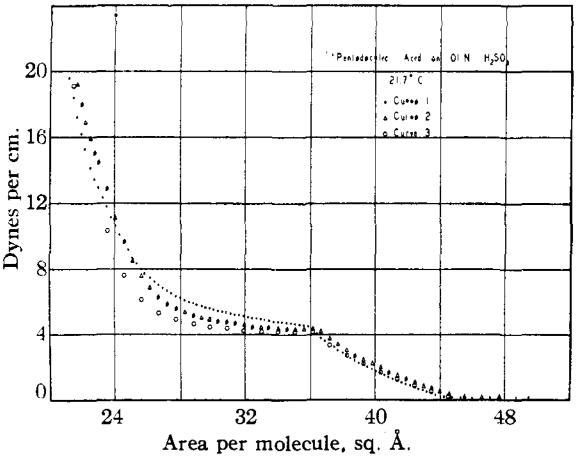

Fig. 4.—Pressure–area relations of pentadecylic acid at 21.7° at different rates of compression. Time elapsed between limiting area at zero pressure and 20 dynes per cm.: Curve 1, 44 min.; Curve 2, 12 min.; Curve 3, 5.5 min.

5. Pressure–Temperature Measurements

Pressure–temperature measurements have been made on monolayers of myristic acid spread on 0.01 *N* sulfuric acid at four molecular areas and on pentadecylic acid films at three molecular areas. Before beginning an experiment the apparatus and subsolution were cooled to the lowest

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(7) D. G. Dervichian, Thesis, Paris, 1936.

temperature desired (2° for myristic, 5° for pentadecylic acid), the surface of the subsolution was cleaned thoroughly and the acid was spread from ligroin solution. The area available per molecule at the time of spreading was always considerably greater than the area at which the measurements were to be made. A period of thirty to fifty minutes intervened between spreading and commencement of the slow compression to the selected molecular area. As soon as the temperature above and below the film differed by only a few hundredths of a degree, determinations of the pressure were begun. Several measurements were made at each temperature and the mean value is reported. The temperature interval was not uniform, amounting to 0.2 to 0.3° at the lowest temperatures and about 0.1° near the transition temperature. Temperatures were read to 0.01°. The experiments were performed slowly, and at such a rate that a period of from four to six hours was used in each experiment.

Each curve in Fig. 6 represents the change with temperature of the pressure of a monolayer of either myristic or pentadecylic acid (Table IV) at a definite, constant molecular area, *e. g.*, 33.2 sq. Å. for myristic acid. At the lowest temperature the pressure is also low for any area investigated, and remains constant to ±0.03 dyne per cm., so the f–T relation is given by a line which is almost horizontal, and represents a film of two dimensional vapor and the islands of aggregated molecules with which it is in equilibrium. At 6.5° the myristic acid film begins to exhibit a rapid rise of pressure with temperature, and a value of $(\partial p/\partial T)_a$ of 0.81. The film is here of the intermediate type. The similar change for pentadecylic acid occurs at 17° and the slope is 1.21 for a = 31.3 sq. Å.

This discontinuity between the pressure of the vapor and that of the intermediate film is in all cases rather sharp and for the three pentadecylic acid films is localized in a small temperature interval near 17.2°. The corresponding discontinuity in myristic acid occurs at a temperature about 11° lower.

Any one of the curves which represents an intermediate film approximates a straight line so closely that the derivative of the slope with respect to temperature may be taken as zero. In the curves of Fig. 6, especially those for smaller areas, departures from linearity are evident, but they are as much in one direction as another and the maximum deviation of the experimental points from the best straight line is of the order of 0.05 dyne per cm.

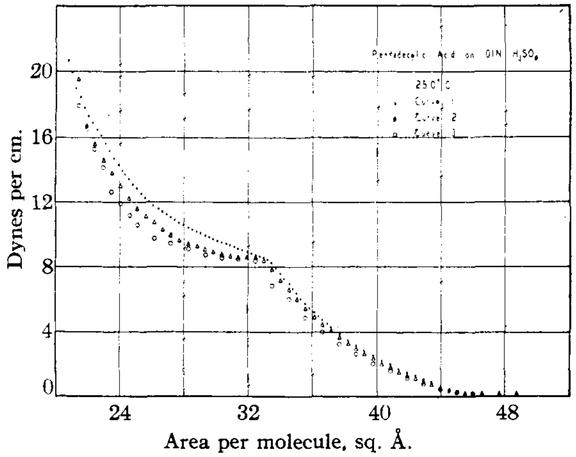

Fig. 5.—Pressure–area relations of pentadecylic acid at 25.0°. Time of compression from limiting area to 20 dynes: Curve 1, 79 min.; Curve 2, 14 min.; Curve 3, 7 min.

The transition Intermediate → Expanded film occurs at a higher temperature and pressure, and seems in some instances to extend over a range of the order of a degree of temperature and a dyne of pressure, but this is dependent upon the rate at which the temperature is increased.

The slope varies from about 0.8 to 1.2 for the intermediate films, but is very much smaller, 0.15 to 0.2, for the expanded films. The f, T relation appears to be linear near the transition region to 0.01 or 0.02 dyne per cm. except where the slope is caused to decrease by the solubility of the film, which increases with both rising temperature and pressure. The solubility effect is exhibited particularly by the myristic acid films above 18°, and especially by the expanded film of this acid at a molecular area of 29.2 sq. Å., since the true positive slope is changed into a fictitious negative one by the increase of solubility.

The slopes $(\partial f/\partial T)_a$ for the intermediate films increase somewhat as the molecular area for a given acid decreases, and are slightly greater for pentadecylic acid, which may be due to the greater solubility of the myristic acid.

The data for the pressure–temperature relations are exhibited in Table III. The temperatures and pressures of transition have been obtained by an extrapolation of the best straight lines which represent the data of the adjacent types of film.

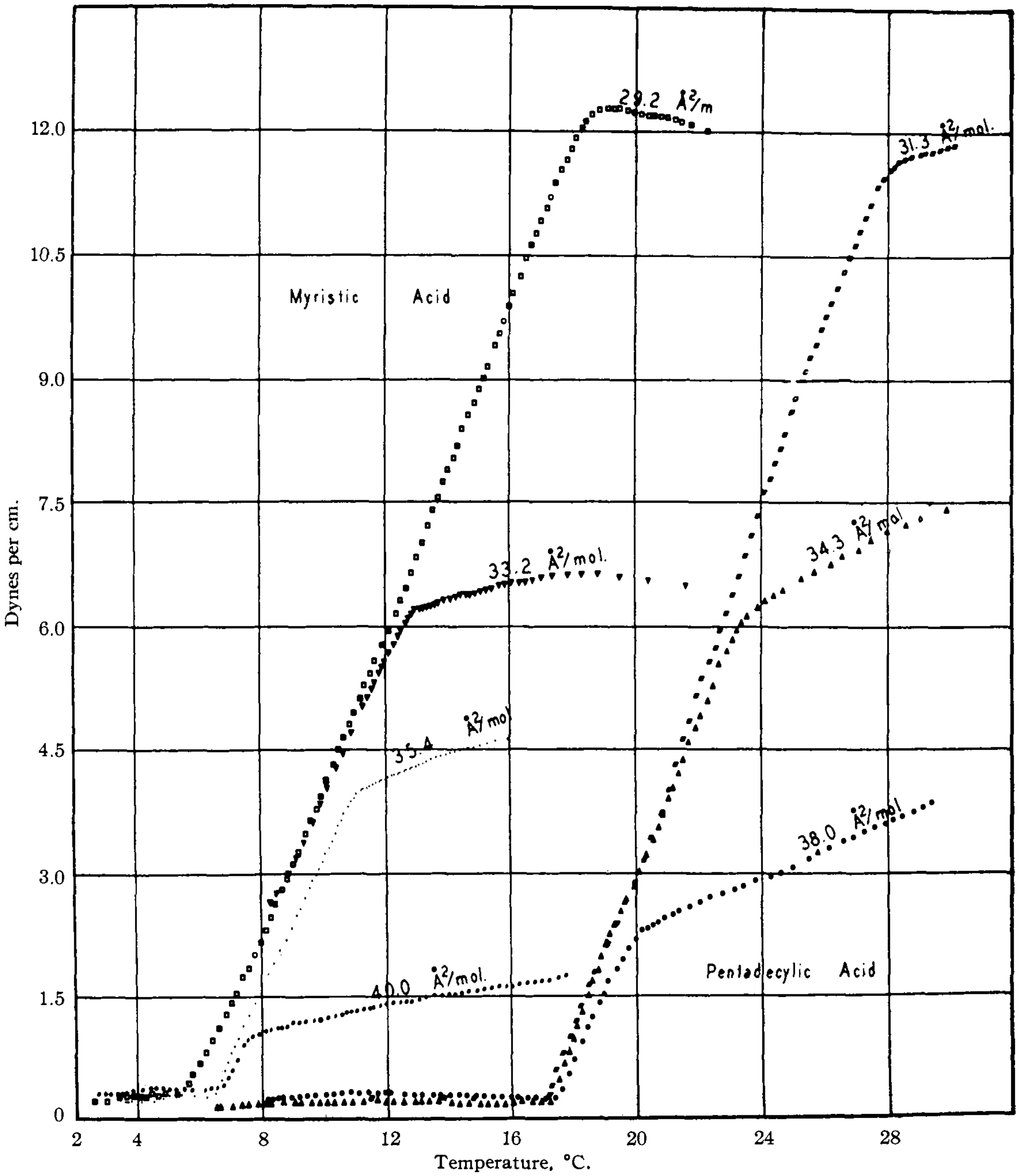

Fig. 6.—Effect of temperature on the pressure of myristic and pentadecylic acid films at constant molecular areas (on 0.01 N sulfuric acid).

6. Transformation of an Intermediate into a Condensed Liquid and into a "Plastic Solid" Film

For many years workers in surface chemistry have assumed that the intermediate may be transformed into a condensed film by increase of pressure, but no such transformation could be detected in the pressure-area plots. However, Harkins and Myers[8] discovered by viscosity measurements that pentadecylic acid undergoes a transformation Condensed Liquid → "Plastic Solid" at 21 sq. Å. and about 23 dynes per cm. No well-defined transformation was apparent in the *f*, *a* curves reported in this paper but Boyd and Harkins found that an extremely great in-

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[8] W. D. Harkins and R. J. Myers, *Nature*, **140**, 465 (1937).

TABLE III

COLLECTED DATA ON MYRISTIC AND PENTADECYLIC ACID FILMS FROM PRESSURE–TEMPERATURE CURVES OF FIGURE 6

Duration of expt., min.	Area per mol., sq. Å.	Slope of branch Dynes per deg., lower	Slope of branch Dynes per deg., upper	Transition temp., °C.	Transition press., dynes/cm.	Expansion temp.	Expansion press., dynes/cm.
			Myristic Acid				
264	29.2	0.932	−0.068	5.5	0.30	18.65	12.32
246	33.2	.828	.113	..	..	12.70	6.16
271	35.4	.800	.163	6.4	.25	10.95	3.97
336	40.0	.719	.0772	6.8	.40	7.72	1.07
			Pentadecylic Acid				
260	31.1	1.05	.091	17.1	.25	27.8	11.60
340	34.3	0.964	.208	17.2	.20	23.4	6.17
269	38.0	.771	.166	17.5	.25	20.1	2.30

crease in viscosity with pressure occurs at a pressure of 21.2 dynes per cm. if the temperature is 25°. After this the pressure–area data were plotted on a different scale (Fig. 7) which revealed the fact that the two straight lines have their intersection at just this point.

The figure seems also to exhibit several additional kink points, but it is unsafe to assume that they represent phase transformations until this assumption has been tested by determinations of the viscosity of these films. Most of the data obtained thus far indicate that there is probably no definite point at which intermediate films are transformed into condensed liquid films.

7. Relation to Theory

Since additional work, with a theoretical bearing, other than that presented here is in progress in this Laboratory, the general discussion of the theory of the expanded and intermediate states will be deferred until later. However, two connections with theory are of moment here.

Langmuir[9] has proposed that the equation of state of an expanded film may be expressed by a van der Waals expression, simplified to the form

$$(f - f_0)(a - a_0) = kT \qquad (1)$$

Here f and a are, respectively, the measured film pressure and molecular area of the monolayer, and the term $-f_0$ is assumed to represent the spreading coefficient (f_S) of Harkins and Feldman[10] for the hydrocarbon oil which would be formed if the polar groups of the substance of the film were to be replaced by hydrogen atoms. For example, if the film is formed from myristic acid, the spreading coefficient should be that for tetradecane. The value of (f_S) is given by

$$f_S = \gamma_w - \gamma_0 - \gamma_{ow} \qquad (2)$$

in which γ represents the surface on interfacial tension and w and o represent water and oil, respectively.

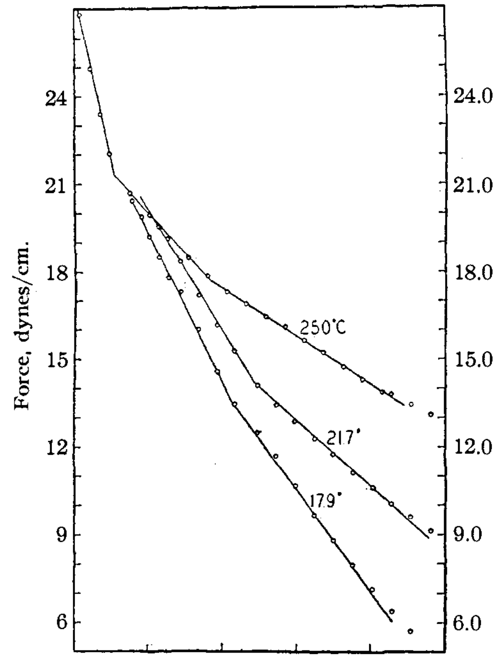

Fig. 7.—Pressure–area relations of pentadecylic acid between 20 and 25 sq. Å. at 25°. Exhibits a phase transition from Condensed Liquid → "Plastic Solid" at 25°, 21.3 dynes per cm., and 20.54 sq. Å. as confirmed by measurements of viscosity.

The values of f_0 which are calculated from the experimental data are seen to vary from 12.3 to 13.0 dynes per cm. for myristic acid, and from 12.4 to 13.5 for pentadecylic acid. While no very accurate determinations of the spreading coefficient have been made, the value for tetradecane obtained by extrapolation from values for the 6 and 8 carbon atom straight chain paraffins

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[9] I. Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).

[10] W. D. Harkins and A. Feldman, THIS JOURNAL, **44**, 2665 (1922).

is about 9, while Langmuir's experimental result is 5.7.

Thus the value of f_0 seems actually to correspond much more closely to the spreading coefficients of long paraffin chains of 17 or 18 carbon atoms in length. The value of the spreading coefficient may be given by another form of Eq. (2) which is

$$f_S = w_A - w_{C_0} \qquad (3)$$

in which w_A is the work of adhesion between the oil and water and w_{C_0} is the work of cohesion of the oil. The next paper of this series, which will give values of f_0 for the 13, 15, and 16 carbon atom acids, should make it possible to show more clearly what the relations are. At present it seems likely that the theory in its use of $-f_0 = f_S$ overemphasizes somewhat the attraction between the hydrocarbon chains and the water. Additional determinations of the value of f_S are needed to ascertain the magnitude of this overemphasis.

The values of a_0 for myristic acid (Table IV) are not constant, but increase with temperature from 12.6 sq. Å. at 12.5° to 14.7 sq. Å. at 25°, so the areas are much too small to agree with those of hydrocarbon chains, since the minimum given by films is 20 sq. Å. and the value given by X-rays is not much less than this.

TABLE IV

VALUES OF THE CONSTANTS a_0 AND f_0 IN THE EQUATION OF STATE FOR EXPANDED FILMS OF MYRISTIC AND PENTADECYLIC ACIDS

Temp., °C.	Area range, sq. Å. per molecule	a_0, sq. Å. per mol.	f_0, dynes per cm.	Root-mean-square devn., dynes per cm.
		Myristic Acid		
12.5	28–50	12.6	12.4	0.46
14.9	30–50	12.4	12.3	.46
16.6	28–50	13.4	13.0	.30
21.7	28–50	14.3	12.7	.53
25.0	26–50	14.7	12.7	.61
		Pentadecylic Acid		
21.7	33–48	14.6	13.5	.21
25.0	31–48	12.0	12.4	.16

In section 4 and Figs. 2, 3, 4, and 5, it has been shown that with intermediate films the product fa increases with the time of compression. That is, in the compression of these films there is a process which takes time for its completion, and this process is in the direction of an expansion with time after any given compression. Thus this process does not seem to be a growth either in size or in number of micelles present in the film, since this would be expected to result in a contraction.

In considering the applicability of Equation (1) to expanded films in general it should be kept in mind that no experimental work as yet done subjects the equation to a critical test. This is due to the fact that although the pressure–area curves approximate rectangular hyperbolas, the approach to the asymptotes is so slow that any curves as yet observed cover only a small fraction of the range necessary to give any uniqueness to this special equation. Thus, with myristic acid at 25° the range covered is only from 30 to 50 sq. Å. and from 0 to 20 dynes per cm. Let it be supposed that the asymptotes lie at $f = -11$ dynes per cm., and $a_0 = 16$ sq. Å. Then in order to approach within 1 dyne and 1 sq. Å. of the asymptotes the respective area and pressure must be 400 dynes per cm. and 400 sq. Å., so the observations extend over only a small part of the curve. At other temperatures the conditions for such a test of the equation are not more favorable.

The extent of the hysteresis observed in the f–a relations of the intermediate state make it difficult to apply Langmuir's theory of this state without a more extensive study of the phenomena involved.

8. Summary

1. The effect of temperature upon the pressure (f) at constant molecular area (a) of monolayers of myristic and pentadecylic acid has been determined. The value of the slope $(\partial f/\partial T)_a$ has been found to be of the order of 0.8 to 1.2 for intermediate, and of 0.15 to 0.2 for expanded films.

2. Pressure–area isotherms for myristic acid have been determined at temperatures from 6.7 to 25°.

3. The compression of intermediate films is found to involve a process which takes time for its completion, and in which at constant temperature the pressure increases with time at constant area, or the area with time at constant pressure.

4. At constant temperature an intermediate film seems to undergo a gradual transition into a condensed liquid film by increase of pressure and the resulting decrease of molecular area. The condensed liquid film exhibits a linear pressure–area relation, and in the case of pentadecylic acid at 25° undergoes a sharp transition to a "plastic" solid film at 21.3 dynes per cm. and 20.52 sq. Å. For any long straight chain molecules the molecular area for the transition Liquid → Solid is very much more independent of the material of the film than the pressure.

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