

Additional confirmation of the ring theory is found in the work of Hartman and Borders.¹³ These authors studied the rate of the acid catalyzed esterification in methyl alcohol of several ortho, meta, and para substituted benzoic acids. They discuss their results with the meta and para compounds on the basis of Hammett's equation for the effect of substituent groups in the meta and para position on the velocity constants of the unsubstituted reactant,¹⁴ but make little mention of the ortho compounds.

The values of the reaction velocity constants for ortho, meta, and para toluic acids show that the latter two esterify with a velocity almost exactly equal to that for benzoic acid, while the ortho-toluic acid esterifies at a slower rate. This is explained readily by the fact that ring formation is possible in the ortho form, but impossible in the meta and para forms.

It would thus appear that the explanation of a ring structure for butyric and higher normal aliphatic acids explains not only the reaction rates

(13) Hartman and Borders, *THIS JOURNAL*, **59**, 2107 (1937).

(14) Hammett, *ibid.*, **59**, 97 (1937).

for the normal acids, but also those obtained with methyl- and phenyl-substituted acids.

Summary

The kinetics of the hydrogen ion catalyzed esterification of the following seven organic acids have been studied: isobutyric, isovaleric, methyl-ethylacetic, isocaproic, phenylacetic, hydrocinnamic, and phenylbutyric.

The results indicate that substitution of a methyl group must take place in the α - or β -position if the reaction velocity is to be affected. Furthermore, the combined effect of completion of a row of four carbon atoms plus substitution of a methyl group on one of these atoms is much greater than that of the substitution alone.

The rate constants for the catalyzed esterification of phenylacetic, hydrocinnamic, and phenylbutyric acids are essentially the same, and but slightly different from those of butyric and higher acids. These are discussed in the light of the postulated ring structure.

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Pressure-Area Relations of Fatty Acid and Alcohol Monolayers

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1. Introduction

This investigation was initiated in order to determine the effect of variations in the length of the hydrocarbon chain upon the pressure-area relations of monolayers. In similar earlier work the temperature of the surface was not controlled with sufficient accuracy because the purity of the compounds was in doubt. Since, however, a considerable number of very pure saturated fatty acids and alcohols have been donated for this purpose by Professor E. E. Reid, it seems worth while to increase the accuracy of the measurements and to include new compounds. Seven acids with fourteen to twenty carbon atoms per molecule, and five alcohols with fourteen to eighteen carbon atoms per molecule, were studied. In order to decrease the solubility of the acid films and to avoid salt formation with multivalent positive ions accidentally present in the subsolution, all of the films were spread on 0.01 *N* sulfuric acid. Measurements of the fatty acids were made

at 25.0° and of the alcohols at 20.0°. At these temperatures myristic and pentadecylic acid films are fully expanded and all the rest of the acids and the alcohols are wholly condensed.

2. Apparatus, Materials and Methods

The film balance used was modelled rather closely after the one described in detail by Harkins and Myers.¹ A few differences may, however, be noted. The accurately threaded rod which moves the barrier which prevents further spreading of the film on the subsolution was usually turned by a hand-operated worm gear of 30 to 1 ratio. The mounting of the worm gear was such that it could be very quickly disengaged from the pinion gear fitted on the threaded rod, when rapid movement of the barrier was desired. A circle divided into 720 parts was mounted on the end of the rod and by means of a counting device whole revolutions of the shaft were indicated.

In order to give better control of the temperature of the surface a new type of trough was constructed. This was machined from a strip of stainless steel, and the inside dimensions were approximately 80 × 25 × 0.5 cm. Attached to the trough was a false bottom through which

(1) W. D. Harkins and R. J. Myers, *J. Chem Phys.*, **4**, 716 (1936).

water from a 350-liter thermostat was circulated. The conditions of flow were so regulated that a film-covered surface in the trough above was disturbed very little. The film balance was enclosed in a box made of aluminum sheet $\frac{1}{8}$ inch (3 mm.) thick and the box in turn was placed in an air thermostat. Two thermocouples of no. 30 constantan and no. 36 copper wire were used to indicate the temperature of the air just above the film and the subsolution just below it. The thermocouples were placed about 1 cm. back of the float of the film balance and by means of screws they could be raised and lowered at will. The couple for measuring the air temperature was about 0.5 to 1 mm. above the surface. The second couple was enclosed in a thin-walled glass capillary tube, 10 cm. of which was well beneath the surface of the subsolution. The sealed end was raised until it was just in the surface. It was assumed, when the temperatures indicated by the two thermocouples differed by no more than 0.1 or 0.2°, that the temperature of the film was known.

An accurate measurement of the vertical lever arm of the film balance requires that the metal float be flat. An error in the length of the vertical arm introduces a proportionate error in all surface pressure measurements. To reduce this error the length of the vertical arm was taken to be the average distance between the point of suspension of the triangular balance beam on the torsion wire and five clearly marked points along the float. The level of liquid in the film trough during this determination was measured and in all subsequent experiments the level was kept exactly the same.

The torsion characteristics of the wire were checked from time to time and in the course of several months did not change sensibly. The calibration curve of the wire was rather accurately linear over the range employed in the pressure-area measurements (0-35 dynes/cm.). As in the apparatus of Harkins and Myers the twist of the torsion wire was indicated on a divided circle connected to the wire through a 20-1 worm gear. One degree on the divided circle corresponded to 0.06 dyne per cm. force on the float, and the circle was read to 0.1°. Successive angle readings usually differed by no more than 0.2 to 0.4°.

Ferric stearate as a material for coating the edges and interior of a film trough has been recommended by Langmuir because it is both oleo- and hydrophobic. It is also superior to paraffin with respect to its higher softening temperature and its superior adhesion to metal surfaces. However, the experiments with ferric stearate were disappointing because of the difficulty of eliminating completely surface active material from the preparation, so its use was abandoned in favor of a high melting paraffin wax applied by moving a cake of the substance over the heated trough. This gave more accurate results.

As solvents from which the films were spread both purified benzene and petroleum ether (60-70° b. p.) were tried. The advantage of benzene is its higher boiling point, which diminishes the concentration change of the solution by evaporation on standing. A greater disadvantage is the slow rate of spreading on 0.01 *N* sulfuric acid at room temperature and below. Frequently lenses migrate to the edge of the trough where, while spreading, they dissolve enough paraffin to vitiate the experiment. Petroleum ether solutions spread very rapidly under the

same conditions and so were used exclusively in the work reported on.

Solutions were spread from a pipet of 0.1 ml. capacity of the type described by Harkins and Anderson.² The preparation and properties of the acids and alcohols are given by Reid and Meyer.³ Water from which the subsolutions were prepared was distilled from alkaline permanganate and condensed in tin. It was free from surface active materials, and the presence or absence of small amounts of metal ions was considered to be of no importance, although their presence was avoided as much as seemed feasible. A series of pressure-area measurements on monolayers of stearic acid spread on 0.01 *N* hydrochloric acid which contained either 0.01 *M* copper nitrate or 0.01 *M* zinc nitrate gave the same results as when stearic acid was spread on hydrochloric acid alone.

After spreading a film a period of ten to fifteen minutes was allowed during which it was assumed that all the solvent would evaporate and any microcrystals or crumpled layers of film material would spread, leaving on the surface of the subsolution only islands of the unimolecular film together with the inevitable film "vapor." The worm gear arrangement referred to earlier was used in compressing the film so that the process was carried out slowly and smoothly. After the films reached an appreciable pressure (*e. g.*, 0.2-0.4 dyne), the decrements of area were for the most part kept constant and the surface pressure at each interval was noted. Above the kink points in the condensed films of both the acids and the alcohols the compressibility is so small that the area decrements were halved. In the case of the alcohols this decrement at the lower pressures was about 0.05 sq. Å. per molecule and in the acids about 0.1 sq. Å. per molecule. Except for Curves 1 and 3 of Fig. 3 the time interval between points was one minute. Compression occupied the first fifteen seconds and the pressure was read at the end of the interval.

The accuracy of the work is difficult to estimate. Determination of the area per molecule involves measurement of the area occupied by a film, preparation of a solution of 25 ml. volume which contains perhaps 30 mg. of solute, and spreading the solution from a pipet whose delivered volume is determined easily within a few hundredths per cent. Since all the operations are capable of high accuracy the determination of the area per molecule of film material would seem also to be highly accurate. Since, as will appear, successive determinations may give areas differing by several tenths of a sq. Å., the limiting factor apparently is the reproducibility of the film itself. Inherently less *accurate* than area measurements are measurements of film pressures, although the *precision* of the determination is obviously high. The question has been considered by Harkins and Anderson.²

3. The Fatty Acids

Figure 1 gives pressure-area curves for four of the fatty acids, margaric and stearic acids being omitted to avoid overcrowding. In Fig. 2 the curves for palmitic and the four higher acids which

(2) W. D. Harkins and T. F. Anderson. *THIS JOURNAL*, **59**, 2189 (1937).

(3) E. E. Reid and J. D. Meyer, *ibid.*, **55**, 1574 (1933).

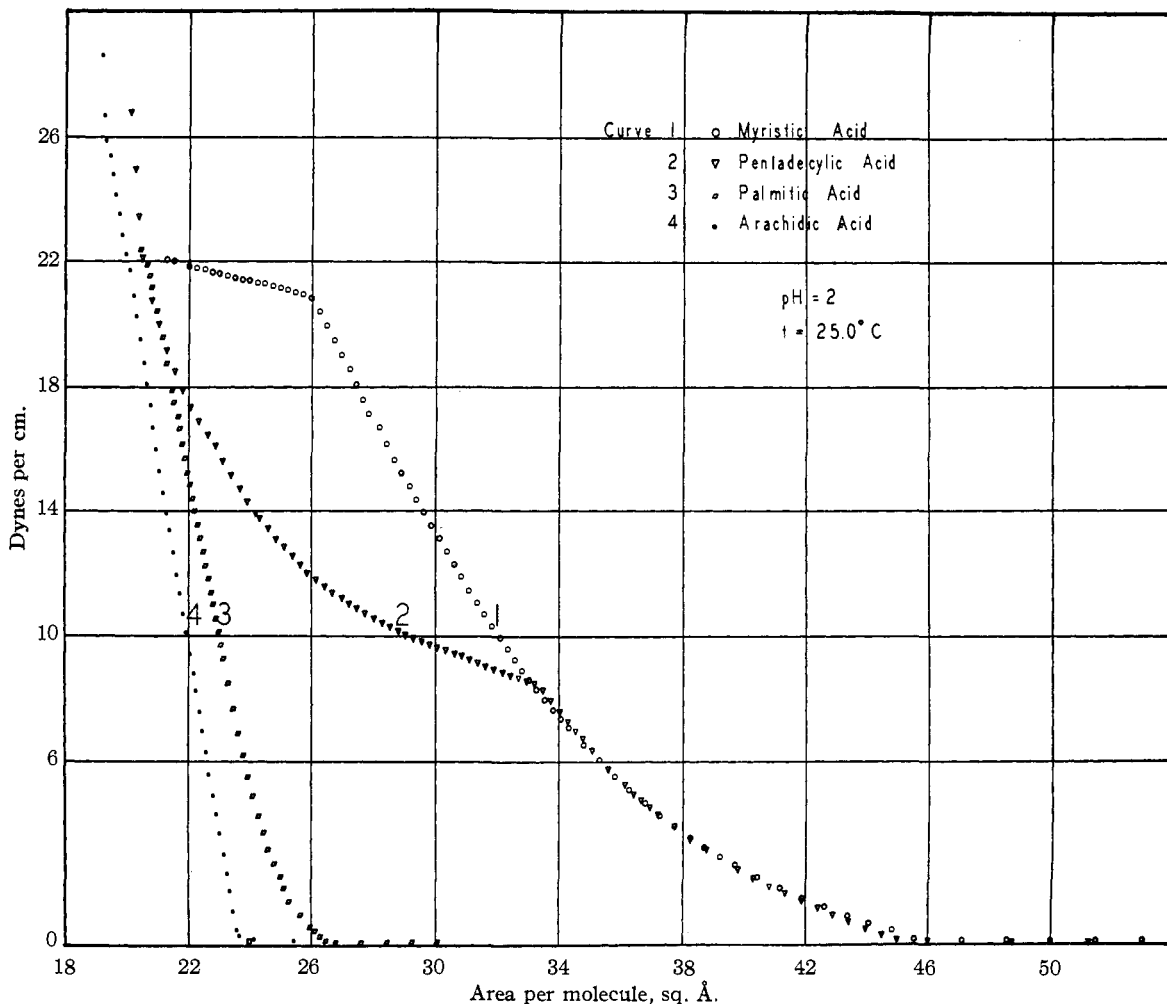


Fig. 1.—Pressure-area relations of the expanded, intermediate, and condensed-liquid films of the fatty acids.

give condensed films at 25° are shown on a larger scale.

The most striking phenomena exhibited by the expanded films of myristic and pentadecylic acids are their great and rapidly changing compressibility both above and below the kink point, the large area at zero pressure and the practically perfect coincidence of the curves below the kink point of pentadecylic acid. This latter relation has not been found in earlier work. Also of note are the sharpness of the break at the kink points and the absence of plateaus above them. If, as has been suggested,⁴ the transition between expanded and condensed films starting at the kink really indicates aggregation of the molecules, it might be expected that on slow compression adequate opportunity for the phase change would be given and the course of the pressure-area curve

(4) I. Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).

would for a time be parallel to the area axis. In actuality, however, although the compression was much slower, the curves are very like the curves for myristic acid obtained by Adam and Jessop.⁵

The next higher acid, palmitic, forms films at 25° much more nearly like the condensed films of the later members of the series. It is, however, in the temperature range of rapid expansion and the form of the curve and the limiting area at zero pressure change very rapidly with only a small increment of temperature. A number of experiments have made it seem likely that to duplicate the pressure-area curve it would be necessary to define the temperature of this film within a few hundredths of a degree.

Films of margaric, stearic, nonadecanoic and

(5) N. K. Adam and G. Jessop, *Proc. Roy. Soc. (London)*, **A112**, 362 (1926).

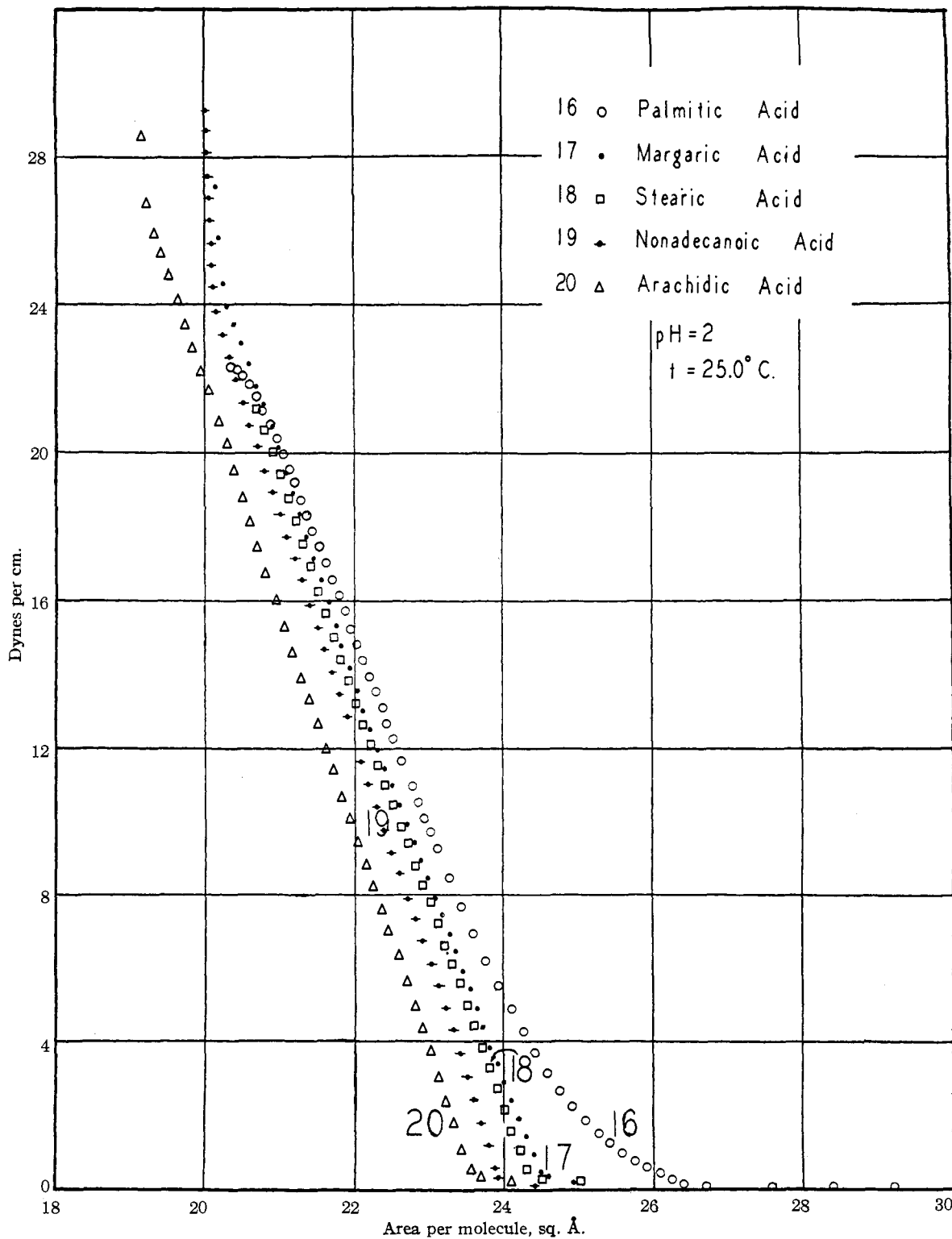


Fig. 2.—Pressure-area relations of condensed-liquid and of "plastic-solid" films of the fatty acids. Values for nonadecanoic acid by Edward Boyd.

arachidic acids are condensed at 25° and a change of temperature during an experiment of several

tenths of a degree is not important. The abruptness with which the curves rise from almost zero

pressure (Fig. 2) indicates, it is thought, the high purity of the samples of fatty acids. Below the kink the plots are very nearly straight lines and are nearly parallel. The lateral displacement of the curves amounts to almost 2 sq. Å. per molecule and is not regular. The area decreases in the series, margaric, stearic, nonadecanoic and arachidic (17, 18, 19, and 20 carbon atoms per molecule) but the difference amounts to only 0.18 sq. Å. between margaric and stearic while it is 0.77 sq. Å. between stearic and arachidic.

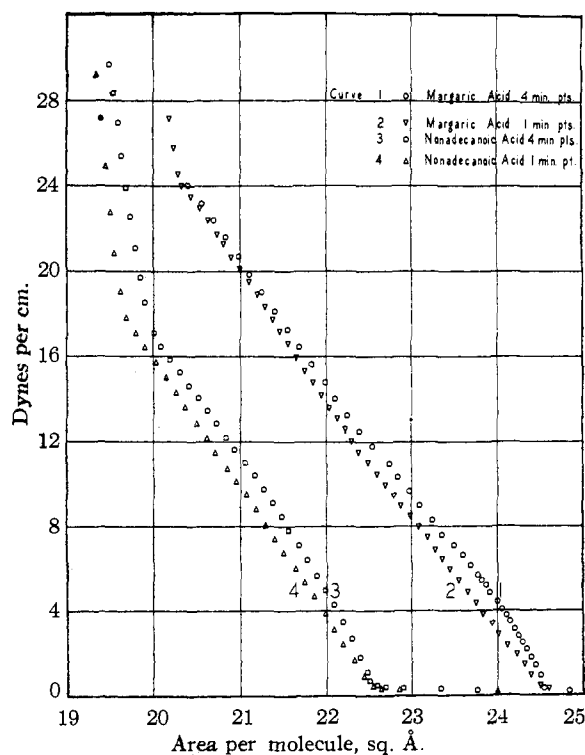


Fig. 3.—Effect of rate of compression on the pressure-area relations of fatty acids. The margaric acid was pure, but the nonadecanoic acid contained an impurity which lowered the molecular area and kink point. The curve in Fig. 2 for this substance is for the purified acid.

Assignment of limiting areas proved to be a difficult task. Most of the features of the pressure-area curves are satisfactorily reproducible. That is, on different days and using different solutions the vapor pressure of the films, the slope of the curves, and the kink-point pressures are much the same. But the limiting areas, which seemingly should be most easily reproduced, varied considerably. To establish values for the limiting areas, therefore, from six to eight pressure-area experiments were made for each acid in the pressure range, 0–6 dynes per cm. The rate of

compression was that given in the preceding section. The average of the extrapolated areas at zero pressure was taken to be the limiting area for the acid in question. Each curve for the condensed films in Figs. 1 and 2, 3 and 4 represents only one complete pressure-area run from zero to collapse pressure but the curves have been moved laterally until the limiting area equalled the average limiting area at zero pressure for the substance. In view of the parallel course of the curves this procedure was deemed permissible.

To illustrate the variability of the limiting areas the results of the individual determinations for four acids and two alcohols are given in Table I. Table II gives the limiting areas for all the acids at 25°, the average slope of the lower limb of the pressure-area curves, the compressibility at 0 and 20 dynes, and the percentage change in the compressibility between zero and 20 dynes.

The compressibilities have been computed from a formula $\left(\frac{-1}{a} \left(\frac{\delta a}{\delta f}\right)\right)$, completely analogous to that used for bulk compressibilities. The sequence of decreasing compressibility is also the sequence of decreasing limiting area, with the curve for margaric acid slightly less steep than for stearic and stearic followed by arachidic and nonadecanoic. The change of compressibility with pressure is, however, nearly constant. The change is an increase and amounts to about 17% in the range 0–20 dynes. It signifies *decreased* resistance to compression with increasing pressure and thus is exactly opposite in sign to the effect observed in three dimensions. A condition of instability is suggested analogous to that leading to film collapse, but slower compression, with four-minute intervals between area decrements and a total compression time of almost two hours for the lower limb of the curves, is not attended by diminished compressibilities.

The effect on pure margaric and impure nonadecanoic acid films of changing the intervals between points from one to four minutes is exhibited in Fig. 3. The four-minute curves start at the same limiting area, begin to rise rapidly at the same pressure, and rise more rapidly up to pressures of about 8 dynes, after which they become nearly parallel to the one-minute curves. Such a time effect, if it exists in films of stearic and arachidic acids, was too small to be detected. With the four-minute intervals on all the five acids (C₁₆–C₂₀) a spontaneous increase in pressure of

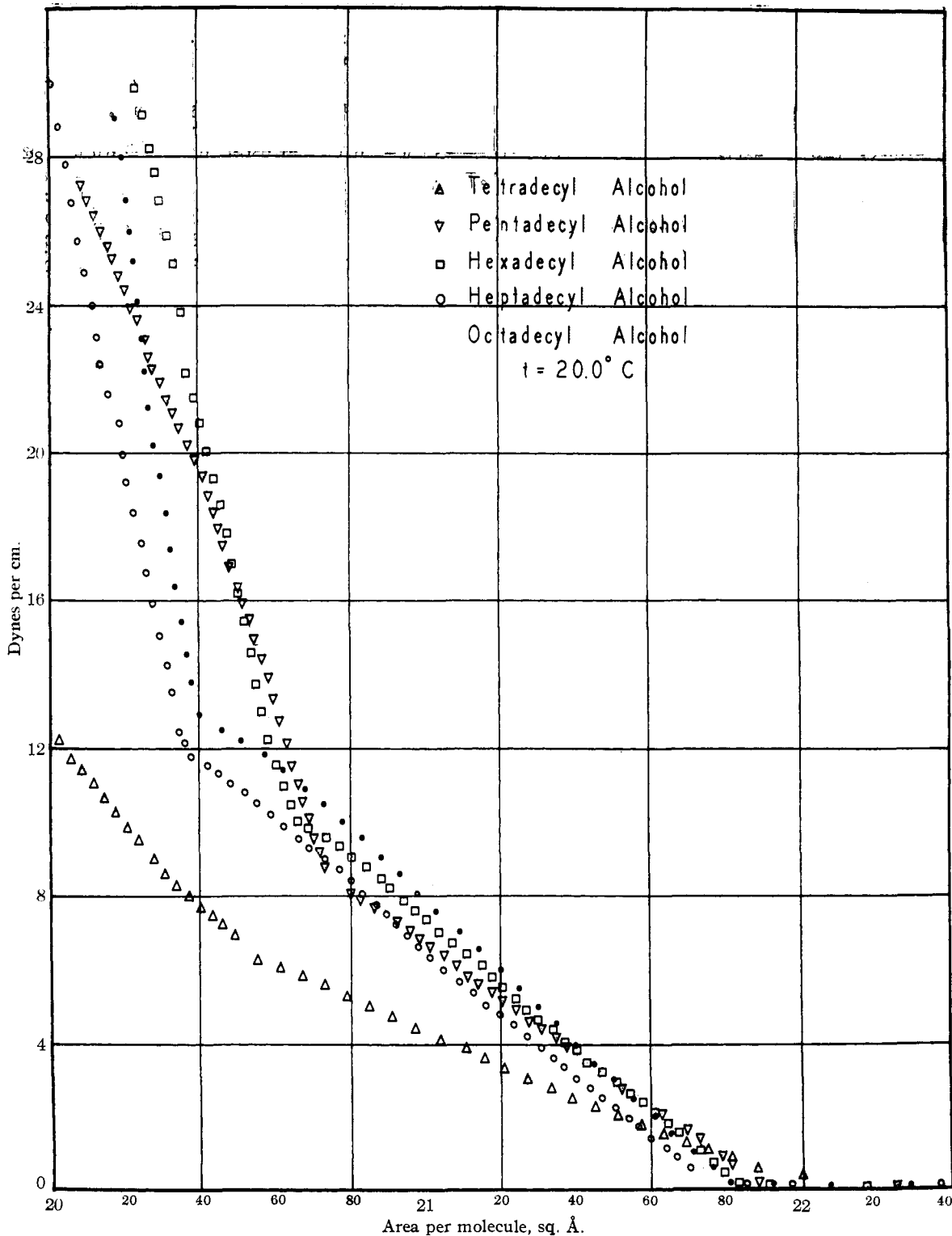


Fig. 4.—Pressure-area relations of condensed-liquid and "plastic-solid" films of the long chain alcohols.

0.03 to 0.1 dynes/cm. during each interval after increase was greatest at pressures near one dyne compression was noted at low pressures. The and diminished to zero at 2 dynes in palmitic and

TABLE I
AREAS AT ZERO FILM PRESSURE FOR LONG CHAIN ACIDS AND ALCOHOLS
Individual determinations in sq. Å. per molecule.

C atoms = 17	Acids			Alcohols	
	18	19	20	15	16
24.60(-0.01)	24.25(-0.16)	24.30(+0.31)	23.61(-0.03)	21.56(-0.35)	21.61(-0.24)
24.50(-.09)	24.66(+.25)	24.02(+.03)	23.87(+.23)	21.77(-.14)	21.96(+.11)
24.25(-.34)	24.43(+.02)	24.20(+.21)	23.63(-.01)	21.95(+.04)	22.03(+.18)
24.75(+.16)	24.20(-.21)	24.02(+.03)	23.60(-.04)	22.12(+.21)	21.79(-.06)
24.68(+.09)	24.35(-.06)	23.47(-.52)	23.46(-.18)	22.08(+.13)	22.17(+.32)
24.73(+.14)	24.37(-.04)	24.17(+.18)	23.66(+.02)	22.09(+.18)	21.76(-.09)
	24.60(+.19)	23.77(-.22)		21.83(-.08)	21.62(-.23)
Av. 24.59 = 0.22%	24.41 = 0.18%	23.99 = 0.30%	23.64 = 0.16%	21.91 = 0.23%	21.85 = 0.25%

TABLE II

Limiting areas of fatty acids at zero pressure on 0.01 N H_2SO_4 at 25.0° (average values). Slope of pressure-area curves (average values). Compressibility of films at 0 and 20 dynes per cm. Change of compressibility in range 0-20 dynes.

C atoms per molecule	Acid	Limiting area (sq. Å. per molecule)	Slope (sq. Å. per dyne)	Compressibility $f = 0; f = 20$		Change of compressibility, %
14	Myristic	46.4
15	Pentadecylic	45.6
16	Palmitic	26.75
17	Margaric	24.59	-0.180	-0.0073	-0.0086	17.1
18	Stearic	24.41	-.177	-.0072	-.0085	16.8
19	Nonadecanoic	24.0	-.163	-.0065	-.0075	15.0
20	Arachidic	23.64	-.159	-.0067	-.0078	16.2

stearic, 4 dynes in margaric and arachidic, and 5 dynes in nonadecanoic acid films.

In films of three of the acids kink-points which separate the pressure-area curves into two segments were observed. Adam considers that the lower segment expresses primarily the closeness of packing of the polar ends of the molecules while the upper segment measures the packing together of the hydrocarbon chains. No kinks were ever observed in palmitic and stearic acid films and in arachidic acid only when the one-minute intervals were used. Evidently here the tendency for film collapse is so strong at pressures in the neighborhood of the kink that more rapid compression is required. The film stability of margaric and nonadecanoic acids proved so much greater that well-defined kinks were observed both with the one- and the four-minute intervals. The kink-point pressure with the margaric acid films was 24 dynes in both cases; with the nonadecanoic acid films, 24 dynes, and with the arachidic acid, 26 dynes.

The upper limbs in all cases were straight lines until collapse set in. The slopes could be determined with some assurance for margaric acid (0.038 sq. Å. per dyne). The upper curves are thus about five times more steep than the lower. It was noted in three cases that at pressures between one-half and one dyne below the kink, the

compressibility of the films increased greatly, but the phenomena did not otherwise resemble true collapse, for the pressure attained on compression did not diminish with time.

Most variable of the film properties was the collapse, since both the pressures and rates of collapse proved so changeable that no generalizations could be made.

4. The Alcohols

Films of the five straight chain alcohols (C_{14} to C_{18}) were spread on 0.01 N sulfuric acid and the temperature was maintained very close to 20.0°. Pressure-area curves are shown in Fig. 4, and Table III gives kink-point pressures, slopes and limiting areas.

All the films are liquid and condensed at room temperature and low film pressure, and display well-defined kinks in their pressure-area curves. The kink-point pressure increases almost linearly with the chain length. Tetradecyl alcohol, with the shortest (14 C) hydrocarbon chain investigated, exhibited a somewhat different behavior, but for the rest of the group the curves are rather accurately linear from about 0.3 dyne per cm. to 0.5 to 1 dyne below the kink, where the slope decreases until the kink is reached. The effect is more noticeable the shorter the length of the chain. As with the acids the increased compress-

TABLE III
 PRESSURE-AREA DATA FOR ALCOHOL MONOLAYERS

Alcohol	Limiting area, sq. Å. per molecule, at $f = 0$		Kink-point pressure, dynes per cm.		Slopes, sq. Å. per dyne		Compressibility	
	Lower limb	Upper limb			Lower	Upper	Lower at $f = 0$	Upper at $f = 20$
Tetradecyl	22.02	21.1	6.2	2.0	0.226	0.084	0.0103
Pentadecyl	21.91	21.0	8.2	2.0	.138	.030	.0063	0.0015
Hexadecyl	21.85	20.9	10.2	1.6	.121	.021	.0055	.00102
Heptadecyl	21.76	20.6	11.8	1.1	.117	.021	.0054	.00104
Octadecyl	21.82	20.6	12.9		.106	.014	.00485	.00070

sibility does not suggest collapse because the film pressure does not fall with time. Above the kink the curves are again linear for several dynes, then slowly bend upward, indicating increased resistance to compression. A quantitative measure of the compressibility of the films at pressures much above the kink is possible only if compression is rapid because collapse begins and masks to a greater or less degree the true compressibility. Unlike the acids, collapse sets in very gradually, denoted by a small decrease in film pressure in the one-minute intervals between compressions. Observations were discontinued when the spontaneous pressure drop in one minute approximated the pressure increase on compression. Except for tetradecyl alcohol this was well above 30 dynes per cm.

The curve of tetradecyl alcohol is linear only up to about 3 dynes, then it curves upward to 5 dynes and quickly turns downward until the kink is reached at 6.2 dynes, where the slope abruptly and markedly increases. The rearrangement beginning near 5 dynes is incomplete at the kink because the pressure drops rapidly, in the one-minute intervals, between 6.2 and about 8 dynes. Above 15 dynes collapse becomes evident.

The limiting area at zero pressure and the slope of the lower limb of the curves have been determined with some accuracy. The values reported are the average of from 7 to 11 measurements. There is a trend toward smaller limiting areas as the chain length increases but it is slight and the difference between the extreme values is less than 0.3 sq. Å. per molecule. Corresponding values for the upper curves have also been tabulated, but the accuracy is much less.

Summary

1. The pressure-area relations have been de-

termined for monolayers of the fatty acids, with from 14 to 20, and of the alcohols from 14 to 18, carbon atoms per molecule.

2. The temperature regulation was more exact than has been attempted previously, to 0.01° in the subsolution and to within 0.1 to 0.2° in the air above it.

3. Contrary to what has been found by others the molecular areas in the condensed liquid films decrease with the length of the hydrocarbon chain. From 16 to 20 carbon atoms the limiting areas at zero film pressure are for the fatty acids, respectively, (26.75), 24.59, 24.41, 24.00, and 23.64 sq. Å. The value in parentheses may exhibit some influence of the intermediate type of film, but the others are truly condensed. This indicates that the van der Waals energy increases with the length of chain, and draws the molecules closer as the intermolecular attraction increases. In the solid plastic state the hydrocarbon chains are so closely packed that the corresponding effect is very small.

4. The limiting molecular areas at zero pressure are for the alcohols at 20° very close to 21.9 sq. Å., and this value is almost constant for hydrocarbon chains between 14 and 18 carbon atoms. The areas of the liquid monolayers at higher pressures are therefore determined by the change from 21.9 sq. Å. as regulated by the compressibility of the film.

5. The pressure of the transition point Liquid \rightarrow Plastic Solid increases from 6.2 dynes per cm. for the 14 carbon to 12.2 dynes per cm. for the 18 carbon alcohol at 20° , but the corresponding values for the acids at 25° are much more constant, since they increase only from 21 to 24 dynes per cm. from 15 to 19 carbon atoms.