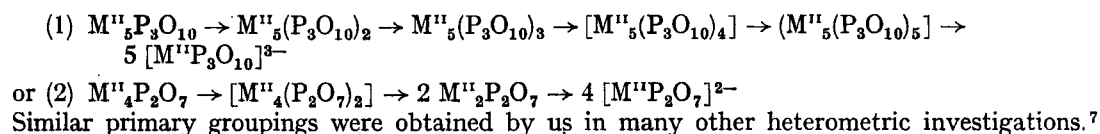In all the cases studied here, two insoluble compounds are obtained which are composed either as $M''_2P_3O_{10}$ or $M''_5(P_3O_{10})_2$. They may be formed by the addition of two or three 'unshielded' cations to the anion complex (VII). The last cation added can only form a regular salt, while the former two may be linked more strongly.

With regard to the intermediate 'primary grouping' which is composed as $[M''_4P_2O_7]^{m+}$ or $[M''_5P_3O_{10}]^{n+}$, both these are formed on the addition of small amounts of sodium polyphosphate to an excess of cations. Every point of attraction of the polyphosphate attracts a single cation. The first nucleus is formed and by further addition of polyphosphate a heterogenous 'chain' reaction occurs as follows:

(1) $M''_5P_3O_{10} \rightarrow M''_5(P_3O_{10})_2 \rightarrow M''_5(P_3O_{10})_3 \rightarrow [M''_5(P_3O_{10})_4] \rightarrow (M''_5(P_3O_{10})_5] \rightarrow$
$5 [M''P_3O_{10}]^{3-}$

or (2) $M''_4P_2O_7 \rightarrow [M''_4(P_2O_7)_2] \rightarrow 2 M''_2P_2O_7 \rightarrow 4 [M''P_2O_7]^{2-}$

Similar primary groupings were obtained by us in many other heterometric investigations.[7]

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# THE INTERACTION OF MONOLAYERS OF BRANCHED-CHAIN FATTY ACIDS WITH CALCIUM IONS IN THE UNDERLYING SOLUTION

### By K. DURHAM

The effect of calcium ions in the substrate on surface films of α-substituted fatty acids has been investigated. It is shown that the introduction of an ethyl group in the α-positions of lauric, myristic and palmitic acids prevents calcium ions from causing surface films of these acids to become solid and brittle at pH 7·5. Fatty acids with main chains longer than $C_{16}$ are found to give brittle solid films on substrates containing calcium ions at pH 7·5.

The effect on the calcium ion/myristic acid film interaction of variation in the size of the substituent group has also been studied and it is found that even a methyl group has sufficient steric hindrance to prevent film solidification.

## Introduction

The effects of metal ions present in the substrate on insoluble monolayers of fatty acids have been observed by many workers.[1-9] A systematic investigation[4] of such systems revealed that calcium ions have a remarkable effect on the mechanical properties of fatty acid monolayers making them rigid and brittle. More recently, Wolstenholme & Schulman[10] have suggested that for substrates containing calcium ions at values of pH greater than 6 the interaction between the fatty acid monolayer and the metallic ions is of the ion–ion kind giving rise to brittle, solid, partially soluble films. These authors[11] point out that the extent of this interaction can be minimised by the introduction of side-groups on the fatty acids, and have studied the interaction between metal ions and monolayers of a few branched-chain fatty acids.

This paper describes a systematic investigation of the effect of the size of the substituted group and the length of the main chain on the interaction between calcium ions and insoluble monolayers of α-branched-chain fatty acids.
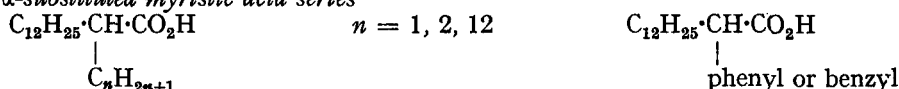
## Experimental

### Materials

Two main series of compounds were used:

(i) *α-ethyl series*

$$C_nH_{2n+1}\cdot CH\cdot CO_2H \qquad n = 10, 12, 14, 16, 18$$
$$|$$
$$C_2H_5$$

(ii) *α-substituted myristic acid series*

$$C_{12}H_{25}\cdot CH\cdot CO_2H \qquad n = 1, 2, 12 \qquad C_{12}H_{25}\cdot CH\cdot CO_2H$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$C_nH_{2n+1} \qquad\qquad\qquad\qquad\qquad\qquad phenyl\ or\ benzyl$$

(These materials were kindly prepared and purified by Dr. B. J. F. Hudson and Mr. J. H. P. Tyman of these laboratories.)

### Techniques

A Langmuir–Adams trough constructed from Monel metal was used in this work and the surfaces of the trough together with the movable barriers were heavily coated with high-melting-point paraffin wax. The effect on the monolayers of any metal ions from the trough which might penetrate the wax and enter the substrate was found to be negligible over the period required to obtain a force–area curve—about one hour. The trough was housed in a double-walled wooden cabinet which contained heaters and thermostat so that the air temperature and hence that of the water in the trough were maintained constant at 20° ± 0·05°. In order to assist temperature stabilisation, movement of the barriers was effected by controls situated outside the cabinet.

The method of measuring surface pressure was developed in these laboratories by Dickenson & Iball,[12] and is essentially a modification of the Wilhelmy plate technique for measuring surface tension in which the ' pull ' on a glass plate immersed in a liquid is measured. In the method employed in this work, a very thin glass plate is attached to a glass buoyancy chamber containing a little mercury; the amount of mercury is adjusted so that when the combination floats in pure water at the appropriate temperature only a few millimetres of the plate project above the water surface. Any change in surface tension causes the float and plate to move vertically and this movement is measured by means of a travelling microscope. A sketch of the float and the Langmuir–Adam trough modified for use with the float is given in Fig. 1. Full details of the construction of the float are given by Dickinson & Iball.[12]

It can easily be shown that the change in height $\delta h$ cm. of the float for a change in the surface tension $\delta \gamma$ is given by:

$$\delta \gamma = \frac{wt g \rho}{2(w+t)} \delta h,$$

where *w* is the width of the glass plate (cm.)
*t* is the thickness of the glass plate (cm.)
*ρ* is the density of the water (g./c.c.)
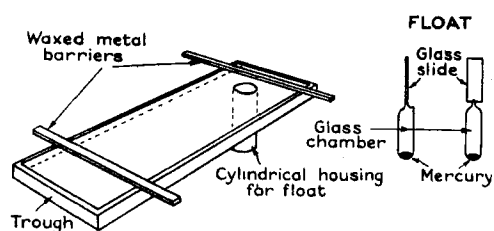*g* is the acceleration due to gravity (cm./sec.²)

FIG. 1. *The Langmuir–Adams trough with housing for float*

In the system used, $\delta\gamma = 500\ t\delta h$ giving a theoretical accuracy of $\pm 0\cdot01$ dynes/cm. In practice, the accuracy was about $\pm 0\cdot05$ dynes/ cm. The advantages of this technique are its simplicity, ease of use and facility of construction of apparatus.

In all experiments the substrate was made up from ' conductivity ' water produced by passing distilled water through a monobed column and the pH was adjusted by saturating with carbon dioxide and adding appropriate quantities of $0\cdot1$ N-NaOH or $0\cdot1$ N-HCl. When M/400-calcium chloride solution was used as a substrate it was made using ' conductivity ' water and A. R. calcium chloride and the pH was adjusted to $7\cdot5$.

The fatty acids were dissolved in redistilled A.R. benzene and were spread on the water from an Agla micrometer syringe. The syringe and all glassware used in this work were cleaned by soaking in a 50/50 mixture of concentrated sulphuric and nitric acids and thereafter rinsing in conductivity water. Precautions were taken to ensure clean water surfaces before spreading the fatty acids. At each stage of compression a period of two minutes was allowed to elapse before the surface pressure was measured.

An indication of the mechanical properties of the films was obtained by gently blowing on to talc particles dusted on to the films. The talc moves freely in a fluid film, but if the film is rigid the talc particles appear to be ' frozen ' in the surface.

## Results

### α-Ethyl series

*Results on a substrate free from metal ions at pH* $3\cdot5$.—The force–area (F–A) curves for the α-ethyl branched-fatty acids on water at pH $3\cdot5$ are shown in Fig. 2. The films were all in the liquid-expanded state at low pressure but α-ethylpalmitic, α-ethylstearic and α-ethylarachidic acids gave films which showed evidence of a transition to a more condensed state as the pressure increased.
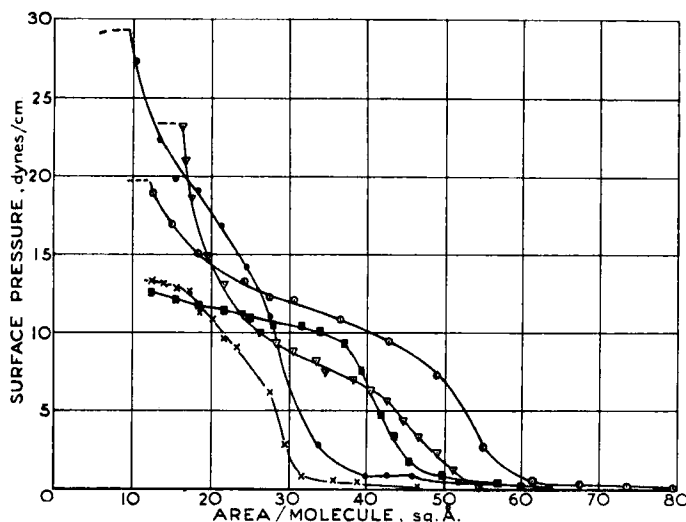


FIG. 2. *Pressure–area curves for films of α-ethyl fatty acids on metal-ion-free water at pH* $3\cdot5$

| | |
|---|---|
| ●———————● | α-Ethylarachidic acid |
| ▽———————▽ | α-Ethylstearic acid |
| ○———————○ | α-Ethylpalmitic acid |
| ■———————■ | α-Ethylmyristic acid |
| ✕— — — —✕ | α-Ethyl lauric acid |

The mobility of talc particles in the surface revealed that the compounds with a main chain containing less than 16 carbon atoms always gave mobile films and showed no tendency to solidify. The branched palmitic and stearic acids, however, gave films which, at relatively high compression, had an elastic or gel-like structure, while the branched arachidic acid gave rigid solid films at high pressures.

It was found that although all the monolayers were fairly stable they exhibited in general a tendency to dissolve slowly on standing; this accounts for the low molecular areas at collapse. In agreement with Stenhagen,[13] it was found that the pressure at collapse fell several dynes below the initial collapse pressure if the monolayer were left to stand for a few minutes.

*Results on* M/400 *calcium chloride solution at pH* 7·5.—The effect of the presence of calcium ions in the substrate on monolayers of the α-ethyl-substituted fatty acids is depicted in Fig. 3. The condensing effect of the calcium ions is at once clear, though it is by no means as great as in the case of straight-chain fatty acids (Table I). At this pH with no metal ions present, all the acids with main chains containing less than 16 carbon atoms would give highly soluble films and even the α-ethylarachidic acid would give a highly expanded film. On hard-water substrates, however, the α-ethylstearic and α-ethylarachidic acids give rigid solid films and the ethyl group is effective in preventing rigidity only for those compounds whose main chain contains less than 16 carbon atoms.

All the surface films were to some extent soluble, α-ethylpalmitic acid and lower homologues giving particularly soluble or unstable films and hence low molecular areas at collapse.

These results are summarised in Table I and compared with results of similar experiments on straight-chain acids; F–A curves for the latter acids are not presented since they are already well known.[14, 15]
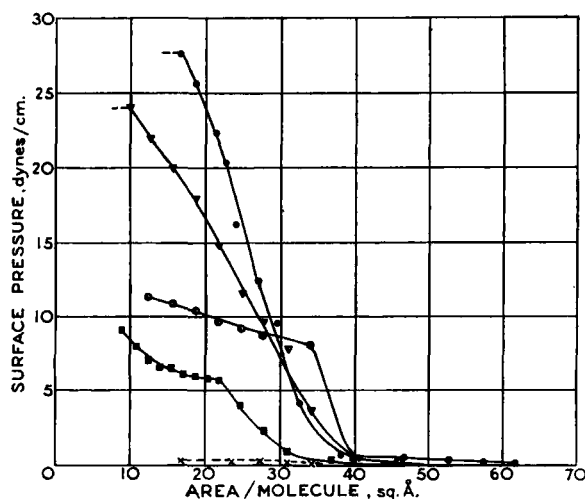


FIG. 3.   *Pressure–area curves for films of α-ethyl fatty acids on* M/400-CaCl₂ *solutions at pH* 7·5

●————● α-Ethylarachidic acid
▽————▽ α-Ethylstearic acid
○————○ α-Ethylpalmitic acid
■————■ α-Ethylmyristic acid
×— —— —× α-Ethyllauric acid

*α-Substituted myristic acids*

*Results on a substrate free from metal ions at pH* 3·5.—The F–A curves for this series shown in Fig. 4 illustrate the effect of varying the size of the substituent group on the nature of the surface film. Almost all the films were liquid-expanded, as indeed is that of myristic acid itself at this pH, the only exception being the film of α-dodecylmyristic acid which approached the gaseous state. All the films remained fluid even at high pressures; the motion of talc particles in the surface gave no evidence of condensation or transition to a more condensed state. The films were also unstable, exhibiting slight solution on compression above about ten dynes/cm.

## Table I

*Comparison of the important features of surface films of branched-chain acids with those of surface films of straight-chain acids*

| Main chain length | α-ethyl fatty acids | | | Straight-chain fatty acids | | |
|---|---|---|---|---|---|---|
| | Area/mol.* at which surface pressure begins to rise | Area/mol.** at closest packing | Nature of film | Area/mol. at which surface pressure begins to rise | Area/mol. at closest packing | Nature of film |
| | (sq. Å) | (sq. Å) | | (sq. Å) | (sq. Å) | |
| $C_{20}$ (*arachidic*): | | | | | | |
| Metal ion-free water pH 3·5 | 60 | 30 | MS | 24 | 21 | S |
| M/400-CaCl$_2$ solution pH 7·5 | 62 | 35 | BS | 21 | 20·5 | BS |
| $C_{18}$ (*stearic*): | | | | | | |
| Metal ion-free water pH 3·5 | 55 | 30 | MS | 25 | 21 | S |
| M/400-CaCl$_2$ solution pH 7·5 | 45 | 38 | BS | 21 | 20·5 | BS |
| $C_{16}$ (*palmitic*): | | | | | | |
| Metal ion-free water pH 3·5 | 80 | 35 | MV | 27 | 25 | S |
| M/400-CaCl$_2$ solution pH 7·5 | 50 | 35–40 | MV | 22 | 20·5 | BS |
| $C_{14}$ (*myristic*): | | | | | | |
| Metal ion-free water pH 3·5 | 63 | 45 | M | 45 | 25 | MV |
| M/400-CaCl$_2$ solution pH 7·5 | 40 | 33 | MD | 22 | 15 (approx.) | SD |
| $C_{12}$ (*lauric*): | | | | | | |
| Metal ion-free water pH 3·5 | 45 | 30 | M | 65 | 27 | MD |
| M/400-CaCl$_2$ solution pH 7·5 | Film completely soluble | | | Film completely soluble | | |

M —Film always fluid.
MD—Film always fluid and slightly soluble.
MV—Fluid film becoming viscous at high pressure.
MS—Initially a fluid film but solidifying at high pressure.
S —Solid film.
BS—Brittle solid film.
SD—Solid film but soluble at high pressure.

* This area gives an indication of the expansion of the monolayer produced by the substituted group at low pressure.

** This area is an indication of the ability of the substituted group to prevent close packing at high pressures.
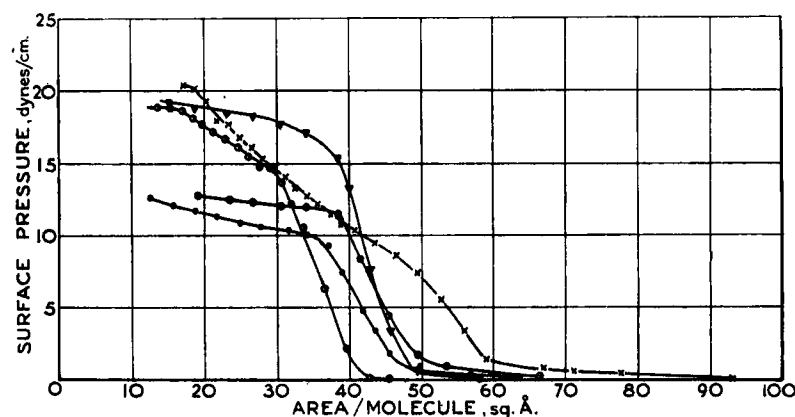


FIG. 4. *Pressure–area curves for films of α-substituted myristic acids on metal-ion-free water at pH 3·5*

O————O  α-Methylmyristic acid
●————●  α-Ethylmyristic acid
▽————▽  α-Phenylmyristic acid
◉————◉  α-Benzylmyristic acid
X– – – –X  α-Dodecylmyristic acid

*Results on* M/400-*calcium chloride solution at pH* 7·5.—On substrates containing calcium ions, only the unsubstituted myristic acid gave rise to a film which was solid, although the

dodecylmyristic acid gave a monolayer which at high pressure behaved like a gel as shown by the reversible displacement of talc particles. All the films were fairly soluble and the rate of compression was highly important. These results are summarised in Table II, and the F–A curves in Fig. 5.

## Table II

*Comparison of the important features of films of α-substituted-myristic acids on metal-ion-free water at pH 3·5 and m/400 calcium chloride solution at pH 7·5*

| Substituent group | Metal ion-free water—pH 3·5 | | | m/400 CaCl₂ solution—pH 7·5 | | |
|---|---|---|---|---|---|---|
| | Area/mol. at which surface pressure begins to rise sq. Å | Area/mol. at closest packing sq. Å | Nature of film | Area/mol. at which surface pressure begins to rise sq. Å | Area/mol. at closest packing sq. Å | Nature of film |
| No substituent group | 45 | 25 | MV | 22 | 15 (approx.) | SD |
| Methyl | 50 | 40 | M | 35 | 23 | MD |
| Ethyl | 65 | 47 | M | 46 | 33 | MD |
| Phenyl | 60 | 50 | M | 60 | 45 | MD |
| Benzyl | 60 | 55 | M | 70 | 45 | MD |
| Dodecyl | 80 | 65 | M | 50 | 33 | MD |

The letters describing the nature of the film are amplified in Table I
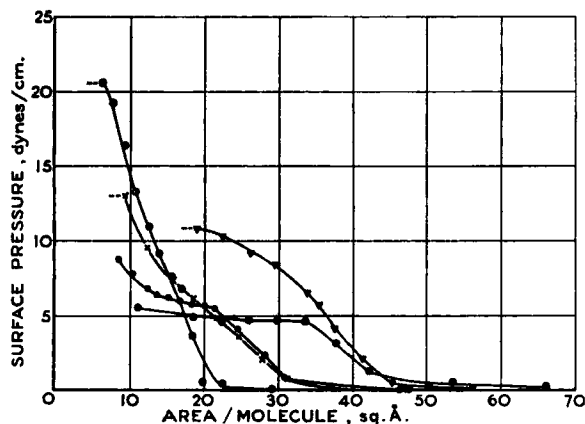


Fig. 5. *Pressure–area curves for films of α-substituted myristic acids on* m/400-CaCl₂ *solution at pH* 7·5

O————O α-Methylmyristic acid
●————● α-Ethylmyristic acid
∇————∇ α-Phenylmyristic acid
O————Θ α-Benzylmyristic acid
X————X α-Dodecylmyristic acid

## Discussion

On a substrate free from metal ions at pH 3·5 an ethyl group substituted in the α-position of a fatty acid introduces sufficient steric hindrance to cause the expansion, at low pressures, of the monolayers of the fatty acids whose main chain contains 20 carbon atoms or less. At high pressures, however, only the monolayers of those compounds with a main chain containing less than 16 carbon atoms remain fluid; the α-ethylpalmitic, α-ethylstearic and α-ethylarachidic acids give films which exhibit a transition to a more condensed state. This indicates that, as chain length increases, the resultant increase in the van der Waal's attraction is sufficient to draw the molecules more closely together. The cross-sectional area for these acids, as deduced from molecular models assuming the two chains to fit tightly together, is 35 sq. Å which is in good agreement with the molecular area at closest packing deduced from F–A curves.

It is also found that, if the length of the main chain is kept constant and the size of the substituent group is increased, the expansion of the monolayers and the areas per molecule at closest packing are progressively increased. The reason why the area at which the surface pressure

begins to rise is a function of the length of the substituent group (Table II) is not clear but it is possible that an increase in the length of the substituent group produces an increase in the angle of tilt of the molecules in the film.

The calcium ions in the substrate have little condensing effect upon the monolayers when the surface pressure is low. This is to be expected since in all the cases investigated the steric hindrance of the substituted group is too great to allow the association of a calcium ion with two fatty acid ions. It has been found[10] that the interaction between calcium and fatty acid monolayers is of the ion–ion type and clearly, the calcium will be unable to link up with the two fatty acid ions if the minimum distance between the carboxyl groups exceeds the bonding distance between the ions. Wolstenholme & Schulman[11] consider that under such circumstances an ionised mono-branched-chain soap exists at the interface, between the molecules of which there exist coulombic repulsive forces. This would account for the fluidity of the films and the fact that they are readily soluble at fairly low pressures. It also appears that an ethyl group is just as effective as a benzyl or a phenyl group in preventing calcium ions from solidifying a myristic acid film.

All the compounds used in this work were substituted in the α-position since it was believed that the nearer the substituent group to the hydrophilic section of the molecule, the more effective the substitution would be in preventing condensation. This belief has been confirmed by the recent work of Izawa[16] who showed that as the substituent group is moved from the α-position to the β- and then the γ-position, the expansion effect produced by similar groups is diminished.

The resistance of branched-chain fatty acid molecules to being packed very closely together in a surface film as shown in this work is also evident in other phenomena. It is reasonable to consider a surface film as a section of an idealised lamellar micelle and, on the basis of the present work, one might therefore expect branched-chain soaps to exhibit a reduced tendency to aggregate as micelles because of the difficulty in packing such soap molecules closely together. Such reduction in the tendency to aggregate has been observed and the increase in the critical micelle concentration produced by branched-chains has been investigated by several workers.[17, 18, 19]

Another aspect of the resistance to packing is that branched-chain salts have rather less surface activity at the same single ion concentration than corresponding straight-chain salts containing a similar number of carbon atoms.[14] This latter effect is, however, somewhat offset by the high critical micelle concentrations of the branched salts which means that high single ion concentrations are possible to give increased surface activity.

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Port Sunlight

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