Surface-Chemical Studies on the Formation of Aluminium Soaps

III. The Interaction between Aluminium Ions and Myristic Acid Monolayers [1,2]

PER EKWALL and HENRIK H. BRUUN

Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland

The conditions promoting interaction between the aluminium ions of potassium aluminium sulphate solutions and myristic acid mono-layers spread on these solutions have been studied with a continuously recording surface balance. The conditions in which the interaction begins, in which it attains a wider scope and in which it leads to a definite endpoint are well-defined and reproducible. The monolayer properties of the aluminium myristate formed by the interaction have been examined. Data characteristic of the monolayers are given.

For our study of the conditions favouring the formation of aluminium soaps from fatty acids, we have chosen myristic acid to represent the latter, particularly as the monolayer properties of myristic acid at various substrate pH values have been previously investigated in detail in this laboratory [3]. In view of the fact that myristic acid forms monolayers of the expanded type at room temperature, it was to be expected that the interaction with aluminium ions would from the beginning be revealed by the condensing effect of these ions upon the monolayers.

The melting point of the myristic acid employed in the study was 54.04° C. The experimental method and the apparatus were the same as those employed previously[1].

MYRISTIC ACID MONOLAYERS AT VARIOUS pH VALUES

The surface pressure-area curves of myristic acid monolayers are well known. A curve recorded on dilute hydrochloric acid (pH 2.5) is reproduced in Fig. 1. The notation used to designate various characteristic points on this pressure-area curve will be employed also in the following.
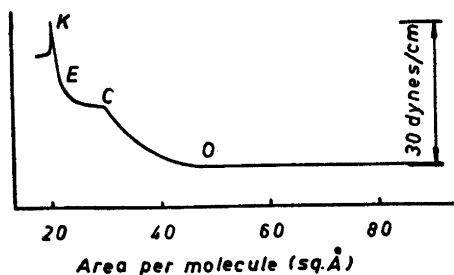
Fig. 1. π—A curve of myristic acid recorded on dilute hydrochloric acid (pH 2.5). 20° C.

Figs. 2a and 2b show how the area and pressure values change when the pH of the substrate is varied (by adding hydrochloric acid and sodium hydroxide; no buffer salts were used in this study).

When the substrate contains no added sodium chloride, most of the area and pressure values remain practically constant up to a pH value of 5.4 (Fig. 2a); only the collapse pressure, π_K, undergoes a slight increase above pH 3.5. On a substrate containing 3 moles of sodium chloride per litre (Fig. 2b), the values remain unaltered up to pH 3.5, except π_K, which begins to increase as soon as the pH rises to 2.5. The changes that occur in the myristic acid monolayers above the pH values mentioned are doubtless connected with the
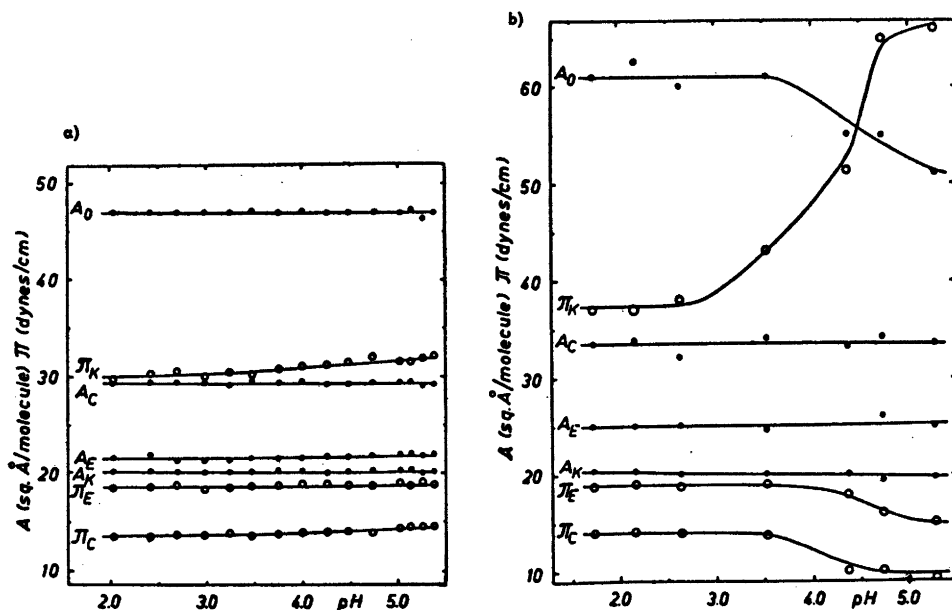

Fig. 2. The dependence of some characteristic points on the pressure-area curves on the pH of the substrate (pH adjusted with dilute HCl or NaOH). 20° C. a. The substrate contains no added sodium chloride. b. The substrate contains 3 moles of sodium chloride per litre.

beginning ionization of myristic acid; these will be discussed elsewhere [3-6]. In Table 1 data are given which characterize the properties of monolayers of undissociated myristic acid under different conditions.

Table 1. Characteristic data for undissociated myristic acid monolayers. The pH of the substrate has been varied by adding HCl or NaOH.

Substrate	Areas per molecule, sq. Å				Surface pressures, dynes/cm		
	A_O	A_C	A_E	A_K	π_C	π_E	π_K
No NaCl added (pH<3.5)	47.0	29.4	21.6	20.2	13.6	18.6	30.4
3 M NaCl (pH<2.5)	63.0	33.5	24.8	20.3	14.0	19.0	37.5

INTERACTION BETWEEN ALUMINIUM IONS AND MYRISTIC ACID MONOLAYERS

a) Substrates containing no added sodium chloride.

The pressure-area curve recordings were made in some cases at constant pH values and with different aluminium ion concentrations, in other cases with constant aluminium ion concentrations and various pH values.

In Fig. 3 are shown a series of pressure-area curves recorded on substrates of pH 3.62 containing various concentrations of potassium aluminium sulphate. At this pH value the monolayer is on aluminium-free substrates almost solely composed of undissociated myristic acid. It is evident from the figure that the expanded pressure-area curve typical of undissociated myristic acid is gradually transformed into a curve of the condensed type as the aluminium ion concentration increases. This transformation is accompanied by a gradual disappearance of the liquid expanded (O—C) and the intermediate (C—E) sections of the pressure-area curve and by a change in the form of the upper part of the curve. This latter change has already occurred in curves 6 and 7, but the middle region of the curve attains its final form (curves 9 and 10) only after the aluminium ion concentration has been increased to 1.6×10^{-3} M. The new curve type does not undergo any further change when the aluminium ion concentration is increased to forty times this value. It is obvious that the changes must be ascribed to the gradual transformation of the monolayer from one containing only myristic acid to one composed of some kind of aluminium myristate, which transformation is complete only after the curve of the new form is fully developed.
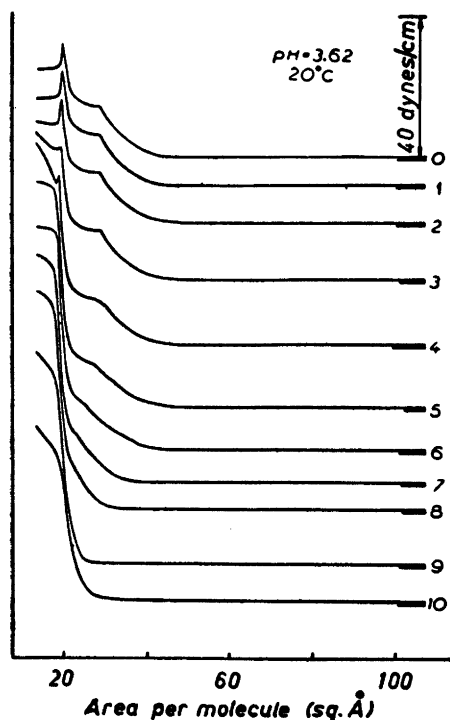
Fig. 3. π—A curves of myristic acid recorded on substrates containing different potassium aluminium sulphate concentrations. pH 3.62. 20° C.

Curve No.	Al concentration moles/litre
0	—
1	$3.0 \cdot 10^{-6}$
2	$1.0 \cdot 10^{-5}$
3	$5.0 \cdot 10^{-5}$
4	$2.0 \cdot 10^{-4}$
5	$4.0 \cdot 10^{-4}$
6	$7.0 \cdot 10^{-4}$
7	$1.0 \cdot 10^{-3}$
8	$1.2 \cdot 10^{-3}$
9	$1.6 \cdot 10^{-3}$
10	$1.3 \cdot 10^{-2}$

The variation of the monolayer properties with increasing aluminium ion concentration in the substrate is shown in Fig. 4. In this figure the values for the various characteristic points on the curves are plotted against the negative logarithm of the aluminium ion concentration.

At the pH value in question, 3.62, the myristic acid monolayer is not affected by the aluminium ions before the concentration of the latter has exceeded ca. 5×10^{-6} M. At this point the collapse pressure, π_K, begins to increase. At higher concentrations it passes through a maximum and finally decreases. At still higher aluminium ion concentrations (about 1.5×10^{-2} M), the collapse pressure again begins to rise.

The values corresponding to the other characteristic points in the curves deviate from those typical of the pure myristic acid monolayer only at appreciably higher aluminium concentrations, at about 5×10^{-5} M. The area per molecule at point 0, A_0, decreases gradually to two-fifths of its initial value, and then begins to increase again at higher aluminium ion concentrations. The point C divides into two separate break points C_I and C_{II}, the former shifting to lower and the latter to higher area values. The surface pressures relating to these points decrease in value, that for the former slowly and that for the latter more rapidly. These break points disappear from the curve completely when the aluminium content of the substrate is increased above 10^{-3} M. Above this
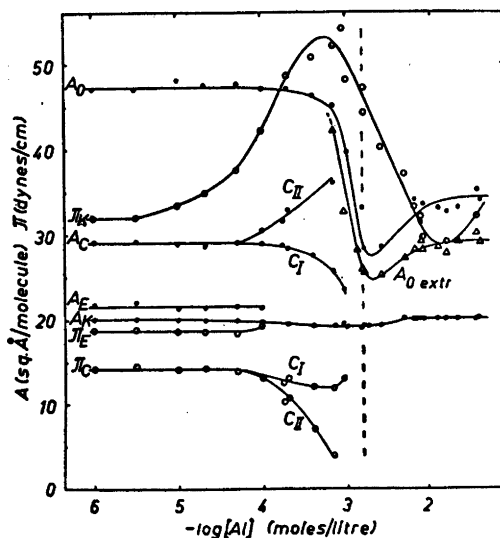
Fig. 4. The dependence of some characteristic points on the pressure-area curves on the potassium aluminium sulphate concentration of the substrate at constant pH 3.62. 20° C.

latter concentration the curve may be considered to comprise only two main parts joined by a short curved section, one which runs almost parallel to the horizontal axis and another which rises abruptly. The value of the extrapolated point of intersection, A_0 extr, changes parallel with A_0 . The collapse area, A_K, varies only slightly, decreases slightly at first but later reverts to its initial value with increasing aluminium concentration.

The monolayer thus undergoes very little change when the aluminium ion concentration is raised to 5×10^{-5} M. Above this latter point there follows an aluminium ion concentration range between 5×10^{-5} and 1.6—2.5×10^{-3} M where the monolayer properties undergo marked variations, but then there follows a range where the monolayer properties vary rather little with the aluminium concentration. In the intermediate concentration range (5×10^{-5}— 2×10^{-3} M) the transition to the new curve type occurs; this type is fully developed at the upper limit of the concentration range.

Several series of experiments were also conducted in which the aluminium ion concentration of the substrate was held constant, but the pH was varied. The data from these series are plotted in Figs. 5—9.

The figures give values for the characteristic points of the pressure-area curves at different pH values up to those where aluminium hydroxide begins to precipitate, *i. e.*, up to the pH values 4.0—5.4 (depending on the aluminium ion concentration). Up to these pH values the properties of a monolayer of pure myristic acid undergo very little change as we have seen above. When aluminium ions are present in constant concentration in the substrate, however, the values for the characteristic points undergo marked variation with
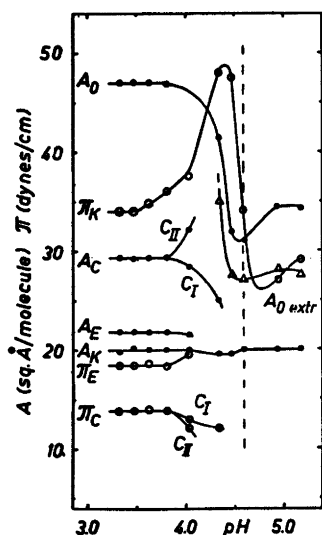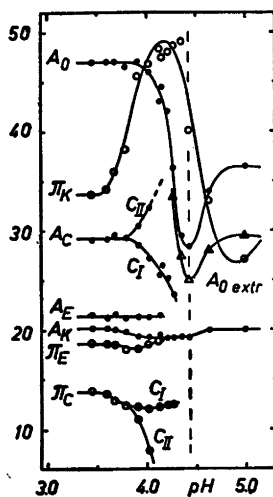
Fig. 5. 6.3 · 10⁻⁶ mole
Al per litre

Fig. 6. 1.0 · 10⁻⁵ mole
Al per litre

Fig. 7. 2.5 · 10⁻⁴ mole
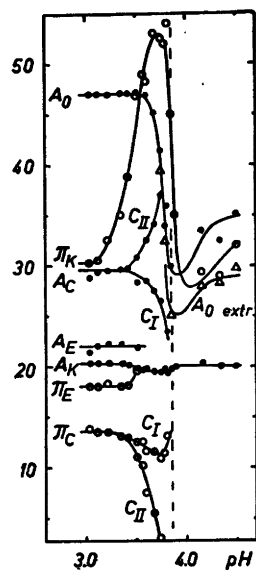Al per litre
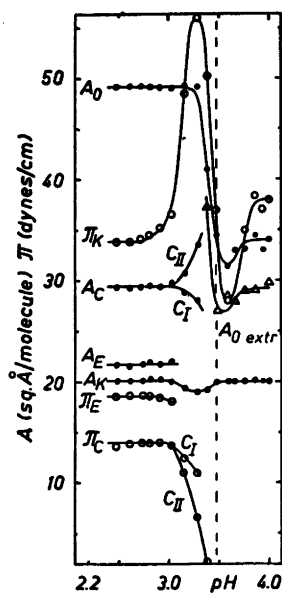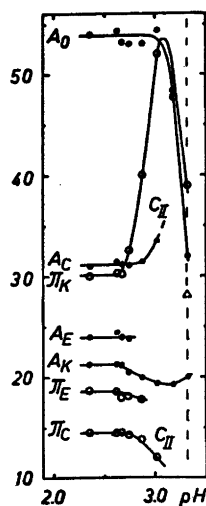
Fig. 8. 1.0 · 10⁻² mole
Al per litre

Fig. 9. 6.0 · 10⁻² mole
Al per litre

Fig. 5—9. The dependence of some characteristic points on the pressure-area curves on the pH of aqueous potassium aluminium sulphate solutions.

Fig. 10. Diagram showing the conditions in which interaction occurs between myristic acid monolayers and aluminium ions in aqueous solutions containing KAl(SO₄)₂. Curves 1a and 1b give the aluminium concentrations and pH values of the substrate when the first signs of interaction between aluminium ions and myristic acid are noted. Curves 2a — 2d connect the aluminium concentrations and pH values at which maximum interaction is observed. Curve 3 gives the aluminium concentrations and pH values at which aluminium hydroxide precipitates in equilibrium conditions. 20° C.
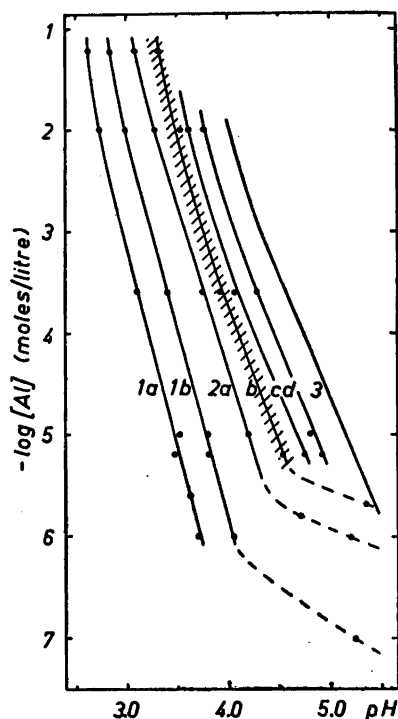
pH, similarly as when the aluminium ion concentration was gradually increased. This shows that the myristic acid monolayer is gradually transformed into an aluminium myristate monolayer when the pH of the substrate is increased. The type of curve characteristic of monolayers of the latter substance is fully developed at the pH values indicated by a dashed line in the figures.

Also in these cases it is the collapse pressure, π_K, that first begins to change; it passes through a pronounced maximum and then a minimum. The other quantities begin to change at pH values that are about 0.2—0.4 unit higher; the greatest variation is shown by the area per molecule at the point 0, A_0, which decreases rapidly to a deep minimum. It is seen that the higher the aluminium concentration, the lower the pH values where the changes occur.

The results of the above experiments on the interaction between myristic acid monolayers and aluminium ions in the substrate are summarized in Fig. 10. The curves 1a and 1b give the conditions at which the first signs of interaction are observed (1a: π_K begins to increase; 1b: A_0 begins to decrease, A_C, π_C and A_K begin to change). The curves 2a, 2b, 2c, and 2d give those conditions at which the maximum changes are noted, *i. e.*, the conditions at which the various quantities attain maximum or minimum values (2a: π_K passes through a maximum; 2b: A_0 decreases to a minimum value; 2c: π_K attains a minimum value; 2d: A_0 increases to an almost constant value). Curve 3 gives those equilibrium conditions at which precipitation of aluminium hydroxide
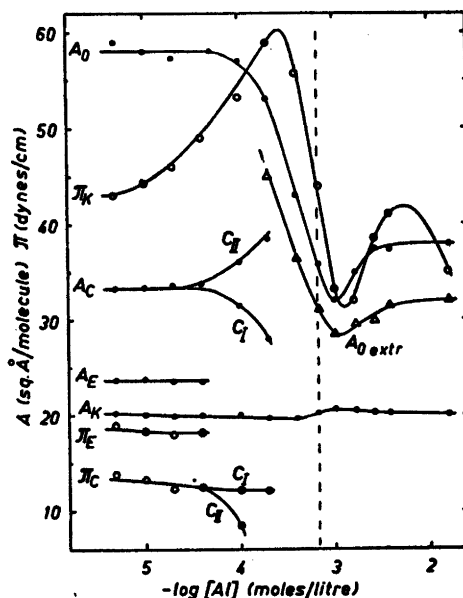
Fig. 11. The dependence of some characteristic points on the pressure-area curves on the potassium aluminium sulphate concentration of the substrate at constant pH 3.60. 20° C. The substrate contained 3 moles of sodium chloride per litre.

begins. The shaded region gives the lowest aluminium ion concentrations and pH values where the fully developed aluminium myristate curve type is observed.

At pH values and aluminium ion concentrations that lie to the left of the curves 1, no interaction has been detected between the aluminium ions of the substrate and the myristic acid in the monolayer. In the region between curves 1 and 2 interaction is reflected in the variation of the different quantities, the greatest interaction taking place within the region between curves 1b and 2b. In the vicinity of the latter curve the monolayer of myristic acid seems to have been completely transformed into an aluminium myristate monolayer.

The full-drawn curves give the conditions in which the interaction is independent of the time that has elapsed before the compression of the monolayer is begun. At low aluminium concentrations the interaction requires some time to attain equilibrium; the dotted parts of the curves 1 and 2 apply to the time of reaction allowed in our experiments, *i. e.*, a total reaction period of five minutes. If the aluminium ions are given a longer time to diffuse to the myristic acid monolayer, the first signs of interaction will be observed at somewhat lower aluminium ion concentrations and lower pH values.
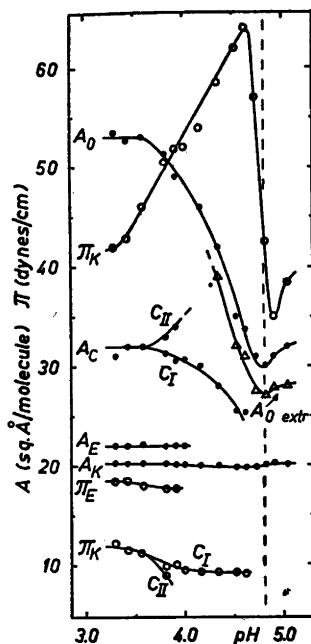
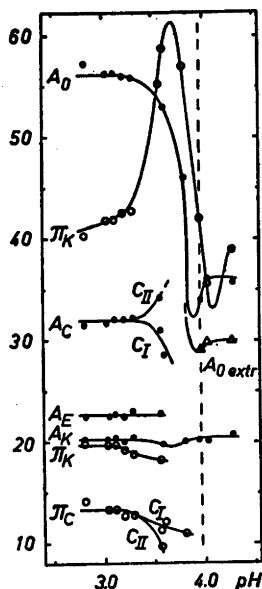Fig. 12. $1.0 \cdot 10^{-5}$ mole Al per litre.

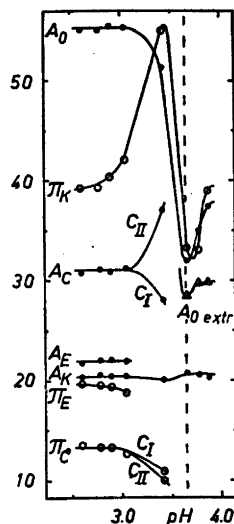Fig. 13. $2.0 \cdot 10^{-4}$ mole Al per litre.

Fig. 14. $1.0 \cdot 10^{-3}$ mole Al per litre.

b) Substrates containing 3 moles of sodium chloride per litre

In order to eliminate the possible effects of the slight solubility of the monolayer substance in the substrate, a series of experiments was conducted employing a substrate containing a relatively high concentration of sodium chloride. The effect of aluminium ions was found to become evident in a similar manner as in the preceding experiments. Fig. 11 shows data obtained in a series of experiments in which the substrate pH was held constant at 3.60 and the aluminium ion concentration was varied. The data given in Figs. 12—16 were obtained in five experimental series in which the aluminium sulphate content of the substrate was constant (at five levels) and the pH was varied. The notation is the same as that used above.

A summary of the experimental data is shown in Fig. 17 which has been drawn according the same principles as Fig. 10. In the range of conditions to the left of the curves 1, no interaction between the myristic acid monolayer and the aluminium ions was detected, while in the region between curves 1 and 2, the interaction was extensive. The greatest changes in the monolayer were observed in the region between the curves 1b and 2b. In the vicinity of the latter curve, the pressure-area curve type characteristic of the aluminium
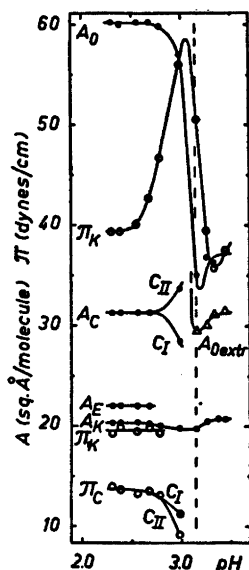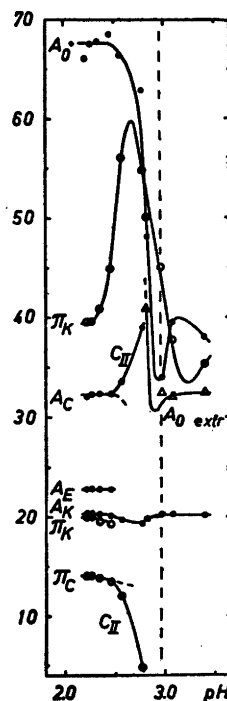
Fig. 15. $6.3 \cdot 10^{-3}$ mole
Al per litre.

Fig. 16. $4.0 \cdot 10^{-3}$ mole
Al per litre.

Fig. 12—16. The dependence of some characteristic points on the pressure-area curves on the pH of aqueous $KAl(SO_4)_2$ solutions containing 3 moles of sodium chloride per litre.

myristate monolayer is fully developed (shaded region), which suggests that the myristic acid has been completely transformed into an aluminium salt.

c) The properties of aluminium myristate monolayers

When interaction takes place between a rosin acid monolayer and aluminium ions of the substrate, all the monolayer properties undergo change almost simultaneously, i. e., when the aluminium ion concentration and the pH attain certain definite values. The same is not the case, however, when a myristic acid monolayer is involved. The various properties characteristic of the monolayer begin to change in succession: the maximum of the collapse pressure, the minimum of the A_0 area and the minimum area at collapse are not attained at the same pH and the same aluminium ion concentration. Neither are the conditions of pH and aluminium ion concentration in all cases the same when the collapse pressure decreases to a minimum and the area A_0 attains a
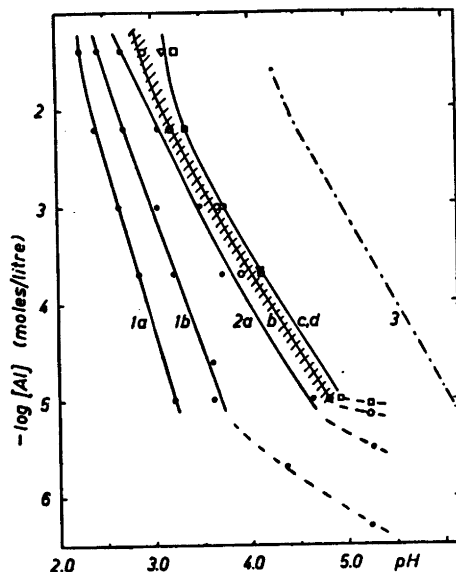
Fig. 17. *Diagram showing the conditions in which interaction occurs between myristic acid monolayers and aluminium ions in aqueous solutions of $KAl(SO_4)_2$ containing 3 moles of sodium chloride per litre. Curves 1a and 1b give the aluminium concentrations and pH values of the substrate when the first signs of interaction between aluminium ions and myristic acid are noted. Curves 2a — 2d connect the aluminium concentrations and pH values at which maximum interaction is observed. (Curve 3 gives the aluminium concentrations and pH values at which aluminium hydroxide precipitates in equilibrium conditions, when the solution contains 2 moles of sodium chloride and $5 \cdot 10^{-2}$ moles of acetic acid-acetate buffer per litre.)*

new fairly constant value at higher aluminium concentrations and pH values. In the case of myristic acid it is therefore more difficult to determine when the reaction goes to completion. This implies either that the reaction between aluminium ions and myristic acid passes through a series of more or less well-defined stages or that the transition of the monolayer properties to those of the final product is complicated by, e. g., steric factors.

As we have seen above, the pressure-area curve type of the aluminium myristate monolayer is in no case fully developed when the collapse pressure, π_K, passes its pronounced maximum. This curve type develops only in those conditions where the molecular area A_0 attains its minimum value. This suggests that the formation of an aluminium myristate monolayer is more clearly indicated by the changes which the properties of a "spontaneously" condensed monolayer, for example A_0 and A_0 extr, undergo than by the changes in the properties of the strongly compressed monolayer, i. e. π_K and A_K.

We hence believe that it is correct to characterize the aluminium myristate monolayer by its properties under those conditions where A_0 attains its minimum value and where A_0 becomes constant.

Table 2. Characteristic data for aluminium myristate monolayers.

Substrate	A. At minimum A_0				B. When A_0 becomes constant			
	Areas per molecule, sq. Å			Surface pressure dynes/cm	Areas per molecule, sq. Å			Surface pressure, dynes/cm
	A_0	A_0 extr	A_K	π_K	A_0	A_0 extr	A_K	π_K
Water, no added sodium chloride (Aluminium ion concentration between $6.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M)	28—32	25—27	19—20	28—42	33—36	28—30	20	27—35
3 M sodium chloride (Aluminium ion concentration between $1.0 \times 10^{-5} - 4.0 \times 10^{-2}$ M)	30—34	27—31	20—21	32—48	33—40	28—33	20—21	33—35

The data in Table 2 have been obtained on substrates with very different aluminium ion concentrations. It is seen that an increase in the sodium chloride content of the substrate leads to larger areas per molecule of monolayer substance and also causes the collapse pressure to increase slightly.

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