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Surface-Chemical Studies on the Formation of Aluminium Soaps

IV. The Product of the Reaction between Aluminium Ions and Monolayers of Myristic Acid

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Monomolecular layers of myristic acid have been spread on substrates containing potassium aluminium sulphate under conditions in which interaction takes place between aluminium ions and the monolayer. The interacted layers have been skimmed from the surface and the content of aluminium in the collected substances has been determined.

The final product of the interaction seems to be a dibasic aluminium monomyristate. Typical aluminium myristate monolayer properties, however, appear already when the aluminium content of the monolayer substance has increased to one mole of aluminium to three to two moles of myristic acid.

In the foregoing paper (Part III[1]) we reported on the conditions in which reaction takes place between a myristic acid monolayer and aluminium ions in the supporting substrate. The lowest aluminium concentration at which the reaction begins varies with the pH of the substrate; those aluminium concentrations in which the reaction proceeds through certain intermediate stages and those in which it attains a definite end-point also vary with the substrate pH. As a result of the reaction the monolayer changes from an expanded to a condensed type. In the following we shall describe the results of our investigation on the constitution of the monolayer substance.

THE ISOLATION AND ANALYSIS OF THE MONOLAYER SUBSTANCE

The monolayer substance was collected for analysis in the same manner as in the case of aluminium monorosinate [2] by skimming the monolayer of myristic acid from the surface of the substrate containing potassium aluminium sulphate. The conditions in which the collection of monolayer substance was performed and the amounts collected are given in Table 1.

The aluminium content of the isolated monolayer substance was determined by the surface-chemical method described in Part II [2] of this series. The carbon and hydrogen contents were determined by micro combustion analysis *.

In all cases the analysed substances were those formed under the conditions where the characteristic surface pressure-area curve for the aluminium myristate was fully developed. The material for analyses 1—3 (Table 1) was collected under conditions where the area A_0 in the pressure-area curve was near its minimum value, material for analyses 4—6 when π_K attained its minimum value and material for analyses 7—8 when A_0 became constant.

Table 1. Data defining the conditions in which the analysed monolayer substances were formed and the results of the analyses.

Analyses No.	Conditions for the formation of the monolayer substances		Number of skimmings	Quantity of monolayer substance in mg	Results of the analyses		
	Al conc. M	pH			Al %	C %	H %
1	$1 \cdot 10^{-2}$	3.43	320	5.2	3.5	65.4	10.4
2	$4 \cdot 10^{-3}$	3.56	320	4.0	3.6	63.6	10.2
3	$1 \cdot 10^{-3}$	3.72	360	6.5	4.6	—	—
4	$1 \cdot 10^{-3}$	3.95	360	8.0	5.9	—	—
5	$1 \cdot 10^{-3}$	3.96	360	11.5	7.0	62.6	10.3
6	$1 \cdot 10^{-3}$	3.96	360	12.0	7.3	61.3	10.5
7	$1 \cdot 10^{-3}$	4.27	360	13.5	9.7	—	—
8	$1 \cdot 10^{-3}$	4.28	360	13.3	10.6	—	—

The samples of the first group were found to contain from 3.5 to 4.6 % aluminium. These values correspond most closely to the aluminium content of aluminium trimyristate (Table 2). For the samples of the second group, the aluminium contents were found to be between 5.9 and 7.3 %, which agrees most closely with the aluminium content of aluminium dimyristate or that of a mixture of the latter salt and aluminium monomyristate. The aluminium contents for the samples of the third group correspond to that of dibasic aluminium monomyristate (Table 2). The carbon contents indicate samples composed of mixtures of di- and monomyristates, while the corresponding hydrogen contents are in close agreement with the hydrogen content of aluminium monomyristate. We are inclined to consider the aluminium determinations most reliable for drawing conclusions about the nature of the monolayer substance.

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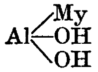
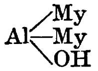
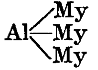
* The latter analyses were performed by Mr. K. Salo at the Chemical Institute of the University of Helsingfors.

Table 2. Theoretical aluminium, carbon and hydrogen contents for different aluminium myristates.

Aluminium myristate	Al %	C %	H %
Dibasic aluminium monomyristate  $\mathrm{Al}\left\langle\begin{array}{l}\mathrm{My}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.$	9.36	58.3	10.3
Monobasic aluminium dimyristate  $\mathrm{Al}\left\langle\begin{array}{l}\mathrm{My}\\\mathrm{My}\\\mathrm{OH}\end{array}\right.$	5.42	67.3	11.1
Aluminium trimyristate  $\mathrm{Al}\left\langle\begin{array}{l}\mathrm{My}\\\mathrm{My}\\\mathrm{My}\end{array}\right.$	3.81	71.2	11.5

THE RELATIONSHIPS BETWEEN THE ALUMINIUM CONTENT AND PROPERTIES OF THE MONOLAYER SUBSTANCE

Despite the uncertainity of the analytical data, these can be taken to indicate that the aluminium content of the monolayer substance increases to one mole of aluminium to three to two moles of myristic acid simultaneously as the pressure-area curve becomes transformed into the form we have considered typical of the aluminium myristate monolayer. Only under the conditions represented by curve 2d in Fig. 10 of Part III of this series does the aluminium content of the monolayer substance as determined by analysis attain the value for dibasic aluminium monomyristate.

Fig. 1 illustrates the relationship between the aluminium content of the monolayer substance and some quantities (A_0 and π_K) defining the monolayer. The quantities defining the monolayer on a substrate containing $1 \cdot 10^{-3}$ mole of aluminium sulphate per litre are plotted against the aluminium contents of the monolayer substance. It is seen from the curves that the properties of the monolayer undergo marked variation until the ratio of aluminium to myristic acid in the monolayer has increased to one mole of aluminium to three to two moles of myristic acid: A_0 diminishes to a minimum, and π_K rises to a maximum value and then decreases. The transformation of the monolayer substance from a substance containing one mole of aluminium to three to two moles of myristic acid to aluminium monomyristate, however, exerts only a slight influence on the monolayer properties; A_0 increases slightly and then remains practically constant, and π_K falls to a minimum value and then undergoes a slight increase.

The data that were considered characteristic of the aluminium myristate monolayer in Table 2, part A (for minimum A_0) in Part III of this series [1] hence apply to the monolayer containing one mole of aluminium to three to

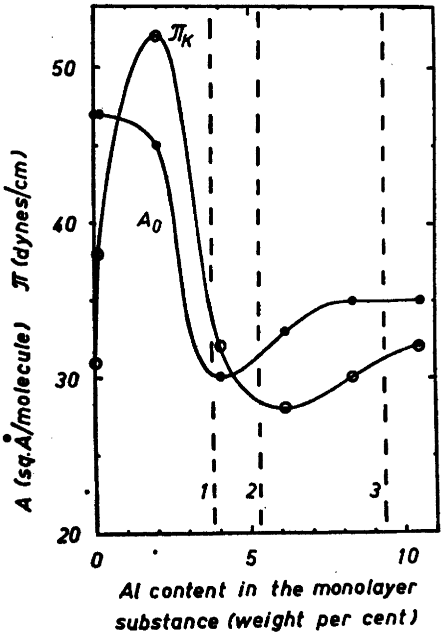


Fig. 1. *The relation between the molecular area* A_0 *and the collapse pressure* π_K *and the aluminium content of the monolayer substance. 20° C. The dotted lines give theoretical aluminium contents for different aluminium myristates: 1 aluminium trimyristate, 2 monobasic aluminium dimyristate, and 3 dibasic aluminium monomyristate.*

two moles of myristic acid and the data in part B of the same table (constant A_0) to a monolayer composed of aluminium monomyristate.

As in the case of the reaction of aluminium ions with a rosin acid monolayer [2], the final reaction product of the interaction between aluminium ions and a myristic acid monolayer is an aluminium soap in which the molar ratio of aluminium to acid is unity. Significant differences are, however, observed in other respects in the reactions of the two acids with aluminium ions. In the case of myristic acid the monolayer attains properties characteristic of the aluminium myristate monolayer already when the aluminium content has increased to one mole to three to two moles of myristic acid. In the case of rosin acid, properties typical of aluminium rosinate become evident only after the monolayer substance has been transformed into aluminium monorosinate.

The reasons for the differences in the reactions of these acids with aluminium ions in the substrate may be connected with the dimensions of the acids and the aluminium ions. The cross-sectional area of the rosin acid molecule is about twice as large as that of the myristic acid molecule. The coulombic forces of attraction due to the positive charges of the aluminium ions immediately below a densely packed monolayer can thus affect the carboxyl groups of a greater number of myristic acid molecules than of rosin acid molecules. It can be estimated that in the compressed monolayer the force of attraction acting on the carboxylic groups of three myristic acid molecules is about twice that on three or two rosin acid molecules. In addition, the great flexibility of the fatty acid molecules makes an intimate interaction between an aluminium ion and several myristic acid molecules easier also in the expanded monolayers. The above-mentioned circumstances perhaps explain why the pressure-area curve typical of an aluminium soap is in one case attained already when the monolayer contains one mole of aluminium for three to two moles of myristic acid but in the other case only when the molar ratio of aluminium to rosin acid is increased to unity. Furthermore it should be noted that the hexaquo-aluminium ion is relatively large in size. The cross-sectional areas of this and of other possible aluminium ions are considerable greater than that of myristic acid molecule but somewhat smaller than that of the rosin acid molecule. Obviously these circumstances play a great part in effecting those changes which the monolayer properties undergo when the rosin acid and myristic acid monolayers are gradually transformed into aluminium rosinate or myristate monolayers and for the differences observed in the behaviour of the two acids in their reaction with the aluminium ions.

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1. Ekwall, P. and Bruun, H. H. *Acta Chem. Scand.* 9 (1955) 412.
2. Ekwall, P. and Bruun, H. H. *Ibid.* 9 (1955) 424.

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