Surface-Chemical Studies on the Formation of Aluminium Soaps

II. The Product of the Reaction between Aluminium Ions and Monolayers of Tall Oil Rosin Acid

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Monomolecular layers of purified tall oil rosin 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, carbon and hydrogen in the collected substances has been determined.

The interaction leads to the formation of dibasic aluminium mono-rosinate. The existence of other aluminium rosinates in the monolayer has not been observed.

In the foregoing paper (Part I)[1] we described a series of surface balance measurements that were planned to define the conditions in which reaction takes place between a tall oil rosin 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 and the reaction attains a definite end-point at a higher aluminium concentration which also depends on the substrate pH. This end-point is signalized by the fact that the changes in the monolayer properties effected by the reaction attain their maximum extent. In the following we shall describe the results of our investigation of the constitution of the monolayer substance.

EXPERIMENTAL

The isolation of the monolayer substance. In order to be able to conduct an analysis of the substance formed by the reaction between the tall oil rosin acid monolayer and aluminium ions it was necessary to collect a sufficient quantity of it. A monolayer of rosin acid was spread in the usual manner on an aqueous potassium aluminium sulphate solution of known concentration and pH. The monolayer substance was compressed to a very small area and removed with suction together with the smallest possible volume of the substrate. New rosin acid was again spread on the substrate and the monolayer substance compressed and removed; this procedure was repeated 200 to 500 times (for different

Fig. 1. π-A curves of tall oil rosin taken at different pH values for the determination of the aluminium ion concentration of the substrate. Curve 1 pH 4.12, 2 pH 4.20, 3 pH 4.28, 4 pH 4.39.
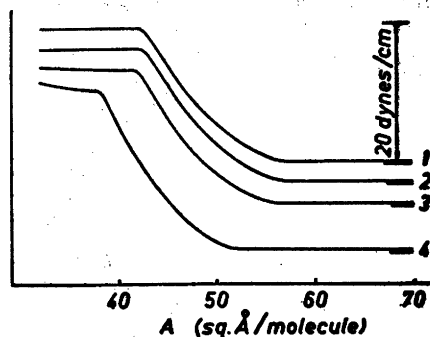
samples). After the monolayer substance had been skimmed off, it consisted of a white flocculent precipitate dispersed in some of the substrate solution. The precipitate was filtered, washed with a few millilitres of water and dried. The quantities of substance obtained in this way varied from 10 to 15 mg.

As the monolayer substance comprised an aluminium rosinate, the concentration of aluminium ions in the substrate was gradually reduced by the above-mentioned skimming procedure. This reduction was especially marked when the aluminium ion concentration was initially low. (In order to maintain the conditions as constant as possible, the substrate was renewed after several skimmings.)

It was established that also the pH of the substrate was altered when the surface layer was removed. In experiments in which the initial aluminium ion concentration was 1.4×10^{-5} M, the pH decreased from the value 5.20 to 5.08. In other experiments in which the aluminium ion concentration was 4×10^{-5} M, the pH diminished during 120 skimmings from 4.80 to 4.60 and 4.50 and in an experiment with the initial aluminium concentration 5.20×10^{-4} M, 240 skimmings lowered the pH from 4.25 to 4.18.

As we wished to know the constitution of the monolayer substance formed under definite conditions, the pH was checked and adjusted from time to time or the substrate was renewed after several skimmings. Since the changes were less marked when the aluminium content of the substrate was not too low, the aluminium concentration was held at 1×10^{-3} M in most of the experiments.

The analytical methods. Carbon and hydrogen in the isolated aluminium rosinate were determined by micro combustion analysis. (These analyses were performed by Mr. K. Salo at the Chemical Institute of the University of Helsingfors.)

The aluminium content was determined by a surface-chemical method developed for the purpose. The principle of the method is the following. 4—6 milligrams of the aluminium rosinate were ashed carefully in a platinum dish and the ash treated with 1—2 drops of concentrated sulfuric acid and some nitric acid. The dried aluminium sulphate was dissolved in water and diluted to a volume (about 1.3 litres) sufficient to fill the surface balance trough. A rosin acid monolayer was spread on this substrate and its pressure-area curve was recorded in the usual manner with the surface balance. The pH of the substrate was adjusted to known values and new pressure-area curves recorded for rosin acid at each pH value. It was found suitable to begin at a low pH value and increase it gradually. The recordings were continued until a definite change in the pressure-area curve revealed that the aluminium ions had begun to interact with the rosin acid monolayer. The data were employed to evaluate accurately the lowest pH value at which the interaction could be detected. Knowing this value of the pH, it was possible to read from curve 1 in Fig. 13 (in Part I of this series) the aluminium ion concentration of the substrate. This procedure could be repeated as many times as desired. The pH of the substrate was altered by adding sodium hydroxide or hydrochloric acid and measured with a valve potentiometer (Radiometer PHM 3) using glass and saturated calomel electrodes.

A number of pressure-area curves recorded during the course of our analyses are reproduced in Fig. 1. No effect of aluminium ions is noted in curve 1 (pH 4.12) and curve

2 (pH 4.20). In curve 3 (pH 4.28), the interaction with the aluminium ions has already become clearly evident; the area A_0 has diminished from 57.0 to 56.2 Å^2 per molecule and the collapse pressure π_K has increased from 19.3 to 19.6 dynes per cm. In general, the pH range in which the effect of aluminium ions was first observed could be determined within ± 0.02 pH units. This permits the determination of the aluminium content of the solution with an accuracy of ± 0.038 units of the logarithm of the aluminium concentration, which corresponds to an accuracy of the analysis of ± 9 %. At first the analyses were conducted using tall oil rosin acid monolayers. Later one of us (Bruun) has employed tetrahydroabietic acid for the purpose, with an increase in accuracy (± 6 %).

Our aluminium analyses were usually conducted in the aluminium concentration range $3 \times 10^{-6} - 3 \times 10^{-5}$ M. The method of analysis cannot be employed with aluminium concentrations under 2×10^{-6} M (See Fig. 13 in part I of this series). It is hence necessary to have at least 0.07 mg aluminium for each analysis when our present surface balance (trough volume 1.3 litres) is used for recordings.

RESULTS

We were particularly interested to determine the constitution of the monolayer formed in the conditions where the surface balance studies indicated that the interaction of aluminium ions and the rosin acid monolayer attained a definite limit, i.e. under those conditions defined by curve 2 in Fig. 13 of the first paper of this series. The analyses 1—4 (see Table 1) relate to monolayer substance collected under conditions close to this curve. The material used in analyses 5 and 6 was collected under conditions to the right of this curve, but under conditions where no precipitation of aluminium hydroxide was yet possible. The conditions in which material for analyses 7, 8 and 9 was collected are represented by points in the region between curves 2 and 1, i.e. in the region where the monolayer has not yet been completely transformed into aluminium rosinate according to our surface balance studies in Part I. In Fig. 2 the mentioned diagram is reproduced and the conditions under which the different samples were collected are marked with circles.

The analyses of all samples of monolayer substance collected when the typical aluminium rosinate pressure-area curve had fully developed gave an

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

| Analysis No.	Conditions for the formation of the monolayer substance		Number of skimmings	Quantity of monolayer substance in mg	The results of the analyses (%)			
	Al conc., M	pH			Al	C	H	Mean values
1	$1.3 \cdot 10^{-5}$	5.07	323	10.8	7.1	68.6	8.92	
2	$3.5 \cdot 10^{-5}$	4.67	240	12.4	7.6	66.8	8.87	7.5 % Al
3	$9.4 \cdot 10^{-5}$	4.50	250	12.6	7.5	66.0	9.04	67.0 » C
4	$5.1 \cdot 10^{-4}$	4.18	240	12.6	—	66.8	8.94	8.94 » H
5	$1 \cdot 10^{-3}$	4.26	360	13.6	7.8	—	—	
6	$1 \cdot 10^{-3}$	4.24	360	14.5	7.7	—	—	
7	$2.1 \cdot 10^{-5}$	4.71	480	13.3	5.4	68.6	8.92	
8	$1 \cdot 10^{-3}$	3.93	330	13.0	3.5	—	—	
9	$1 \cdot 10^{-3}$	3.88	220	10.0	3.3	—	—	
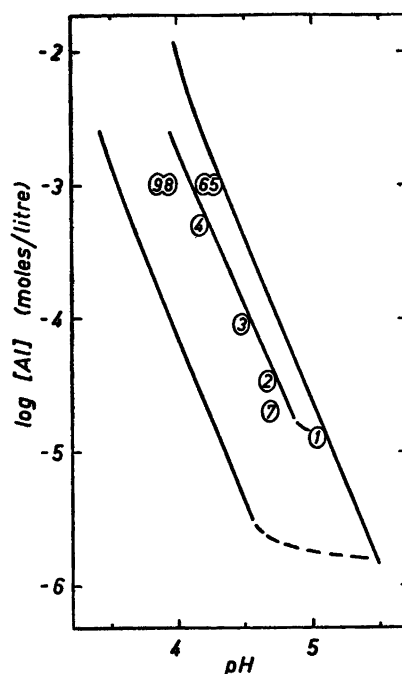
Fig. 2. Schematic diagram showing the conditions in which the monolayer samples were taken. The numbers refer to Table 1, the curves correspond to those in Fig. 13 of the first paper in this series.

aluminium content exceeding 7 %. The monolayer must hence have been converted into an aluminium monorosinate. The mean aluminium content, 7.5 %, corresponds closely to that calculated for a dibasic aluminium monorosinate, 7.44 % (Table 2). Also the carbon content is in agreement with that

Table 2. Theoretical aluminium, carbon and hydrogen contents for different aluminium rosinates (%).

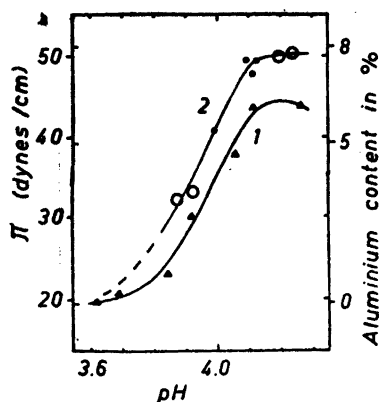| Aluminium rosinate	Al	C	H
Dibasic aluminium monorosinate Al $\diagup$ Ros Al—OH $\diagdown$ OH	7.44	66.3	8.56
Monobasic aluminium dirosinate Al $\diagup$ Ros Al—Ros $\diagdown$ OH	4.17	74.3	9.13
Aluminium trirosinate Al $\diagup$ Ros Al—Ros $\diagdown$ Ros	2.70	77.3	9.34

Fig. 3. The collapse pressure π_K (Curve 1) and the aluminium content (Curve 2) of tall oil rosin acid monolayers on substrates of different pH values containing $1 \cdot 10^{-3}$ mole/l of $KAl(SO_4)_2$. 20° C. (The pH values of the points on curve 2 were found by interpolation).

of aluminium monorosinate, but the hydrogen values deviate somewhat more and are between the values for the mono- and dirosinate.

Analyses 7—9 have given results which show that the monolayer substance in question corresponds to an aluminium rosinate of low aluminium content. The aluminium content decreases with the pH of the substrate on which the monolayer was formed i.e. the more the conditions differ from those yielding the aluminium rosinate pressure-area curve. It falls down to and below the aluminium content of monobasic aluminium dirosinate.

In order to give a clear picture of how the properties of the monolayer vary with its constitution, the curves in Fig. 3 are reproduced. Curve 1 in Fig. 3 shows the changes of the collapse pressure with pH on substrates containing 1×10^{-3} mole aluminium per litre. Curve 2 gives the aluminium content of the monolayer substance formed on solutions of the same composition. (The circles give experimentally determined aluminium values. In those cases where the monolayer substance has been collected on solutions of lower aluminium content than $1 \times 10^{-3} M$, the corresponding pH value on the substrate mentioned has been interpolated from the curve 2 of Fig. 13 in Part I.) The point
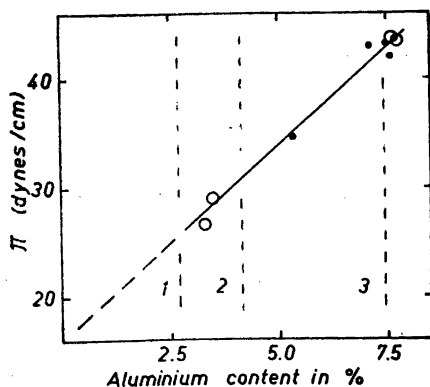

Fig. 4. The relation between the collapse pressure π_K and the aluminium content of the monolayer on substrates $1 \cdot 10^{-3}$ M in $KAl(SO_4)_2$. 20° C. The dotted lines give theoretical aluminium content for different aluminium rosinates. 1 aluminium trirosinate, 2 monobasic aluminium dirosinate, 3 dibasic aluminium monorosinate.

where the properties of a typical aluminium rosinate curve are fully developed and the aluminium content of the monolayer substance is that of the dibasic aluminium monorosinate becomes clearly evident. Up to this pH value, both curves run continuously.

Fig. 4 shows directly the variations of the collapse pressure of the monolayer with its aluminium content. There are no break points in the curve up to the aluminium content of the dibasic aluminium monorosinate. The conclusion thus seems justified that the reaction between aluminium ions and the rosin acid monolayer takes place without intermediate stages until the formation of aluminium monorosinate is complete and that the latter compound is the final product of the primary interaction. Before this end-point is reached, the monolayer is evidently a mixture of unreacted rosin acid and aluminium monorosinate.

REFERENCE

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