

Surface-Chemical Studies on the Formation of Aluminium Soaps

I. The Interaction between Aluminium Ions and Rosin Acid Monolayers

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A continuously recording surface balance has been employed to study monomolecular layers of purified tall oil rosin acid on substrates of varying acidity and containing different amounts of potassium aluminium sulphate. The conditions promoting interaction between the monolayer substance and aluminium ions in the substrate have been investigated in detail in the presence of 2 *M* sodium chloride and without added salt. The monolayer properties of the aluminium rosinate formed by the interaction have been examined.

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 aluminium rosinate formed has characteristic and constant monolayer properties.

In the year 1948 the present authors began a series of investigations with the object of defining the conditions which promote interaction between aluminium ions in aqueous solution and rosin acid spread in a monolayer on the surface of the solution. Up to the year mentioned most of the numerous investigations that had dealt with the formation of aluminium soaps had involved reactions in three-dimensional systems¹⁻¹¹. Only a few observations in this respect had been made using surface-chemical methods¹²⁻¹⁴.

In our investigations we established¹⁵ that by means of the surface balance technique it is possible to determine rapidly and in an elegant manner the conditions favouring such interactions. The same technique was then employed in a study of the interactions between aluminium ions and fatty acid monolayers^{16,17}. These studies have later been extended to reactions between aluminium ions and the surfaces of solid rosin acid and solid fatty acids which were examined by another surface-chemical method, the measurement of contact angles^{16,17}. This latter work confirmed, for instance, that the results obtained with the aid of the monolayer technique are of general significance. At approximately the same time as our first results were reported, Schulman

and coworkers published the results of their work on metal-monolayer interactions in aqueous systems in which they employed a similar technique to solve problems of a similar nature¹⁸⁻²¹.

It is our intention to describe our investigations in a series of articles under the main title of this paper.

MATERIALS AND METHODS

The investigations described below were made with tall oil rosin acid because of the great technical importance of this material.

The rosin acid was prepared from crystalline tall oil rosin from Enso-Gutzeit Oy., Kotka, Finland. According to Juvonen²², this product comprises 94.7 % rosin acids, 4.8 % unsaponifiables and 0.07 % ash; its melting range is 160–165° C. At Oy Keskuslaboratorio – Centrallaboratorium Ab, Helsingfors, the unsaponifiables and fatty acids were removed by extraction, the latter after esterification, and remaining rosin acids were recrystallized from ethanol. The melting point of this product was 166–169° and the mean equivalent weight 301. We then purified this product by the method of Aschan³. The substance was ground to a powder and allowed to remain for 20 hours under 80 % ethanol. The undissolved rosin acids were recrystallized twice from pure methanol and once from acetone. The rosin acid remaining melted in the range 168–174° C (corr.). The optical rotation $[\alpha]_D^{20}$ in absolute ethanol varied from –33° to –43° for different samples (measured with a Lippich polarimeter using a 2 dm tube, the concentration being about 0.01 g/ml).

Tall oil rosin acid is a mixture of different rosin acids²⁴. According to Sanderman²⁵ it comprises about 50 % abietic acid, about 25 % dehydro-, dihydro- and tetrahydroabietic acids and about 25 % dextropimaric acid. Harva²⁶ has spectrophotometrically followed the purification of the Enso-Gutzeit tall oil rosin acid by recrystallization in the above-mentioned manner and found that the abietic acid content first rises to a level of 43 % but then remains fairly constant on further recrystallization.

Aschan and coworkers²⁷⁻²⁹ established that the tall oil rosin acid mixture prepared in the above-mentioned manner behaves in many respects as a single rosin acid. This was to some extent confirmed by Harva³⁰ in respect of the physico-chemical properties of tall oil rosin soap in aqueous solution. Later studies in this laboratory with synthetic mixtures of pure rosin acids have shown that this is also the case in respect of the surface-chemical properties³¹ and that the properties of the individual acids greatly resemble those of the tall oil rosin acid³².

The rosin acid was dissolved in benzene (concentration, $2 \cdot 10^{18}$ molecules per ml). In order to prevent the oxidation of the abietic acid, the solution was stored in a glass-stoppered flask in a benzene atmosphere; fresh solutions were frequently prepared.

The rosin acid-benzene solution was added from an Agla micrometer syringe to the surface of the aqueous substrate in a Langmuir trough and the properties of the rosin acid monolayer formed investigated by the aid of an automatic, self-recording surface balance of Wilhelmy-Dervichian type^{33,34} (improved by Anderson-Groth, Stållberg-Stenhagen and Stenhagen³⁵). Compression of the monolayer was begun 2–3 minutes after the rosin acid had been spread on the surface; the rate of compression was 7–12 cm per minute.

When the effect of hydrogen ion concentration on the monolayer was studied, the pH values of the substrates were measured with a glass electrode and a saturated calomel reference electrode. The standard EMF was checked against phosphate buffer solutions.

TALL OIL ROSIN ACID MONOLAYERS AT DIFFERENT pH VALUES

Tall oil rosin acid monolayers give surface pressure-area curves (Fig. 1) that are of the same type as those obtained for the dextropimaric acids and tetrahydrodextropimaric acid by Harkins, Ries and Carman^{36,37}. Both

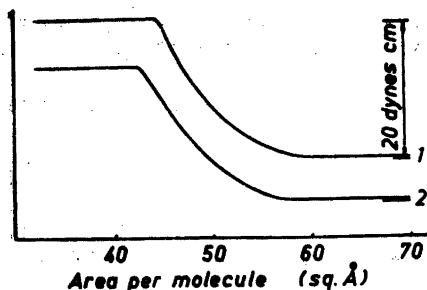


Fig. 1. π -A curves of tall oil rosin acid recorded on dilute hydrochloric acid (pH 3). 20° C. 1 The substrate contains no sodium chloride, 2 The substrate contains 2 moles of sodium chloride and $5 \cdot 10^{-3}$ moles of acetic acid-acetate buffer per litre.

on pure water and on 2 *M* aqueous sodium chloride solution, the monolayers are of the liquid condensed type.

Fig. 2 shows the variation of certain characteristic points on the surface pressure-area curves with the pH of the substrate. A_0 denotes the area per molecule in the monolayer when the pressure first begins to rise, A_K the area per molecule at the point where the monolayer collapses and π_K the surface pressure at this point. (The collapse point is determined by extrapolation.) The mentioned quantities remain practically unaltered on acid substrates up to pH 4.2–4.6. Above this pH, the areas per molecule begin to decrease and the pressure to increase. It is obvious that at pH values below this limit, the rosin acid molecules are undissociated. The changes in the monolayer properties observed above this pH limit are evidently due to the inception of ionization in the monolayer. In Table 1 data characteristic of undissociated tall oil rosin acid monolayers are given.

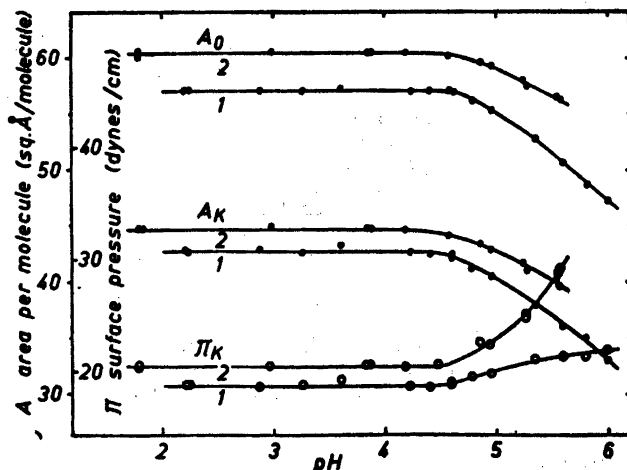


Fig. 2. The values of A_0 , A_K and π_K for different pH values of the substrate. 20° C. 1 The substrate contains no sodium chloride, 2 The substrate contains 2 moles of sodium chloride and $5 \cdot 10^{-3}$ moles of acetic acid-acetate buffer per litre.

Table 1. Characteristic data for undissociated tall oil rosin acid monolayers (below pH 4.2–4.6).

Substrate	A_0 Å ² per molecule	A_K Å ² per molecule	π_K dynes/cm
Water; pH adjusted with dilute HCl	57.1	42.7	19.4
2 M NaCl, buffered with $5 \cdot 10^{-2}$ M acetic acid-acetate	60.2	44.6	20.4

On the 2 M sodium chloride solution the molecules in a rosin acid monolayer take up an area about 2–3 Å² larger than on pure water. The pressure that the monolayer can withstand before it collapses is about 1 dyne/cm larger in the former case.

On pure water the ionization becomes evident in the monolayer properties in the pH range 4.4 to 4.6 and on 2 M sodium chloride in a slightly lower pH range between 4.2 and 4.5. The ionization results in an increase of the solubility of the rosin acid. It is, however, difficult to determine to what extent this increase of the solubility leads to a transfer of rosin acid ions from the monolayer into the substrate. It is also difficult to determine if the observed decrease in the area per molecule is caused only by this dissolving process. The fact that the collapse pressure increases slightly in this pH range shows that the mentioned area decrease is not solely attributable to the dissolution of the monolayer substance even in the case of pure water. On the 2 M sodium chloride substrate, in which the solubility of the monolayer substance is lower than in water, the decrease of the area per molecule is less and the increase in collapse pressure considerably larger than on pure water.

THE INTERACTION BETWEEN ALUMINIUM IONS AND TALL OIL ROSIN ACID MONOLAYERS ON 2 M SODIUM CHLORIDE

The surface balance method can be employed to define those conditions in which interaction between aluminium ions and rosin acid monolayers can and cannot take place. An interaction will lead to changes in the properties of the monolayer which will become evident in the form of the surface pressure-area curve¹⁵. This is shown by the curves in Fig. 3 which refer to tall oil rosin monolayers spread on substrates 2 M in sodium chloride and containing different concentrations of aluminium ions. In all cases the hydrogen ion concentration was regulated to pH 4.00 by means of an acetic acid-acetate buffer. Curve 3,0 is a recording taken when the substrate contained no aluminium ions, and curve 3,1 refers to a substrate containing $4.92 \cdot 10^{-5}$ mole of potassium aluminium sulphate per litre. No effect of aluminium ions is evident in the latter curve. As soon as the aluminium concentration is increased to $1.17 \cdot 10^{-4}$ M (curve 3,2), however, the curve undergoes a slight change; both A_0 and A_K decrease. These changes become more marked with increasing aluminium ion

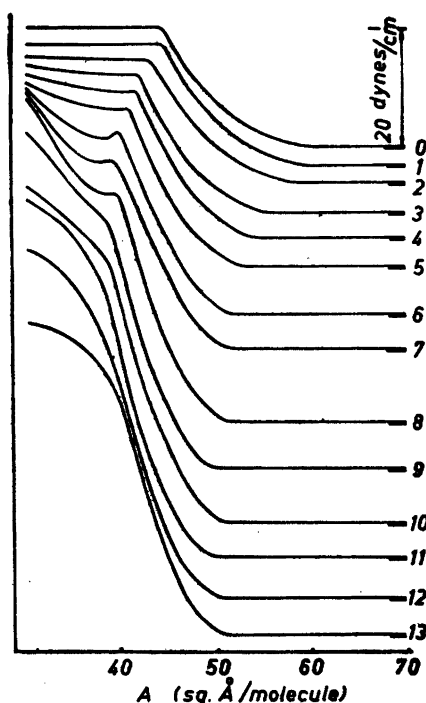


Fig. 3. π - A curves of tall oil rosin acid recorded on substrates of pH 4.00 containing 2 moles/l sodium chloride, $5 \cdot 10^{-3}$ moles/l acetic acid-acetate buffer and different potassium aluminium sulphate concentrations.

Curve No.	Al conc. moles/litre	Curve No.	Al conc. moles/litre
0	—	7	$5.00 \cdot 10^{-4}$
1	$4.92 \cdot 10^{-5}$	8	$6.14 \cdot 10^{-4}$
2	$1.17 \cdot 10^{-4}$	9	$9.22 \cdot 10^{-4}$
3	$1.78 \cdot 10^{-4}$	10	$1.05 \cdot 10^{-3}$
4	$2.21 \cdot 10^{-4}$	11	$1.17 \cdot 10^{-3}$
5	$3.08 \cdot 10^{-4}$	12	$1.86 \cdot 10^{-3}$
6	$4.32 \cdot 10^{-4}$	13	$5.02 \cdot 10^{-3}$

concentration; at the same time the curve shifts upwards and the collapse pressure π_K attains a higher value. The curve type passes through several intermediate stages from the original type to an altogether new type. This new type is fully developed in curve 3,12. When the aluminium ion concentration is increased further, this type remains constant; only the height of the curve diminishes slightly.

Values of A_0 , A_K and π_K have been measured from a larger series of recorded curves of which those shown in Fig. 3 are representative. The variation

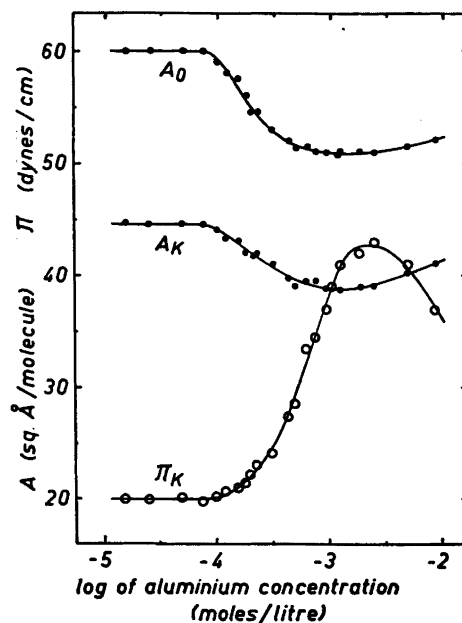


Fig. 4. The dependence of A_0 , A_K and π_K on the potassium aluminium sulphate concentration of the substrate at constant pH 4.00 \cdot 20° C. The substrate contains 2 moles of sodium chloride and $5 \cdot 10^{-2}$ moles of acetic acid-acetate buffer per litre.

of these quantities with the aluminium concentration is shown in Fig. 4. It is seen that when the pH of the substrate is held at 4.00, the tall oil rosin acid monolayer is unaffected by aluminium ions until the concentration of the latter exceeds $8.9 \cdot 10^{-5}$ M. Higher aluminium ion concentrations bring forth changes in the curves and hence in the structure of the monolayer itself. Each variation in the aluminium ion concentration effects definite reproducible changes in the monolayer properties. The previously mentioned new curve type is fully developed when the aluminium ion concentration is about $1.8 \cdot 10^{-3}$ M. The collapse pressure has increased from 20.4 dynes per cm to more than double this value, 42.6 dynes per cm. The interaction between the rosin acid molecules in the monolayer and the aluminium ions in the substrate gradually leads to an exchange of the monolayer substance from one of pure rosin acid to one composed of an aluminium rosinate, and this exchange seems to be complete at the aluminium ion concentration $1.8 \cdot 10^{-3}$ M. The new curve type is characteristic for monolayers composed of this aluminium rosinate. When the aluminium ion concentration is increased above the last-mentioned value, the aluminium rosinate layer undergoes further changes which become evident in the pressure-area curves: the collapse pressure π_K decreases again slowly and the areas per molecule, A_0 and A_K , increase gradually.

We have conducted a similar series of experiments in order to determine the effect of increasing the aluminium concentration at several pH-values. Some of the results are illustrated in the form of curves of the same type as in Fig. 4. Fig. 5 thus shows the effect on A_0 , A_K and π_K of increasing aluminium ion concentration at pH 3.77, Fig. 6 at pH 4.32, Fig. 7 at pH 4.54, Fig. 8 at pH 5.00 and Fig. 9 at pH 5.60. In all cases the interaction between the

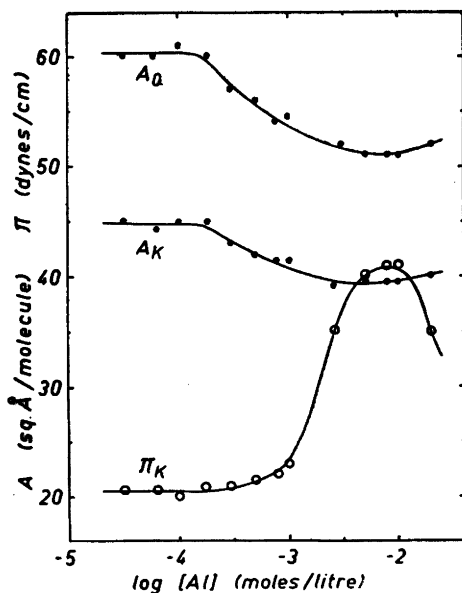


Fig. 5.

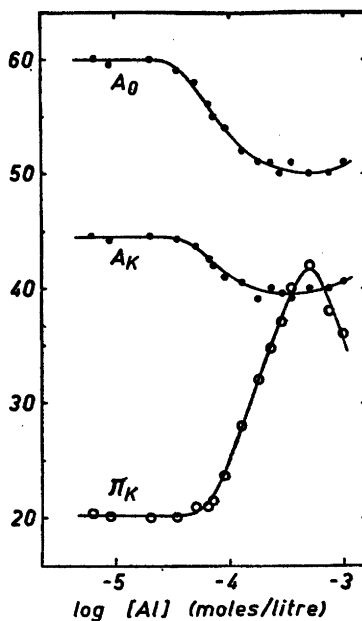


Fig. 6.

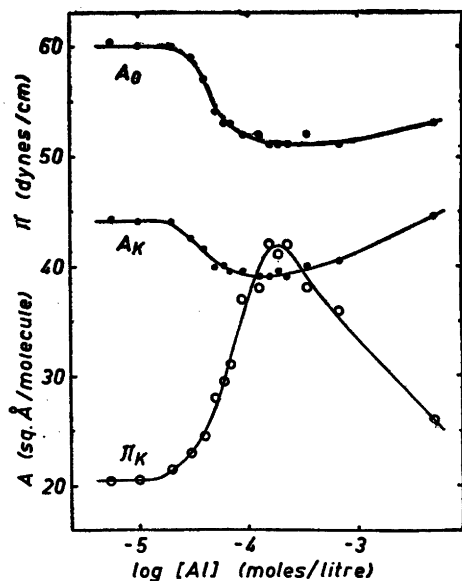


Fig. 7.

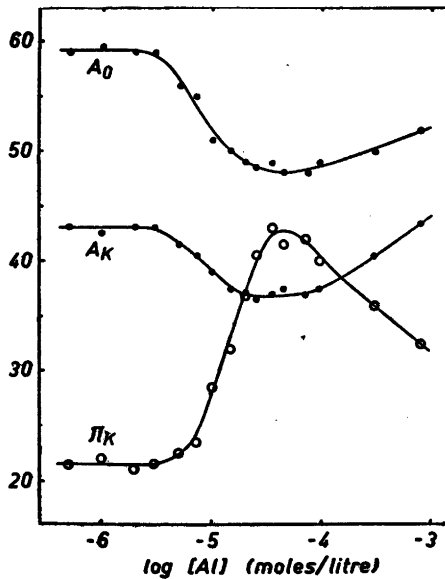


Fig. 8.

Figs. 5–9. The dependence of A_0 , A_K and π_K on the potassium aluminium sulphate concentration at constant pH. The substrate contains 2 moles of sodium chloride and $5 \cdot 10^{-3}$ moles of acetic acid-acetate buffer per litre. Fig. 5 pH 3.77, Fig. 6 pH 4.32, Fig. 7 pH 4.54, Fig. 8 pH 5.00 and Fig. 9 pH 5.60.

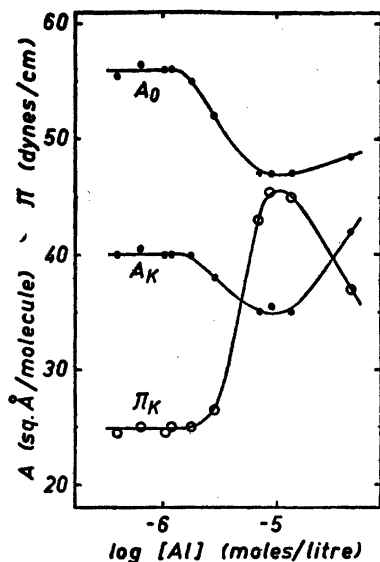


Fig. 9.

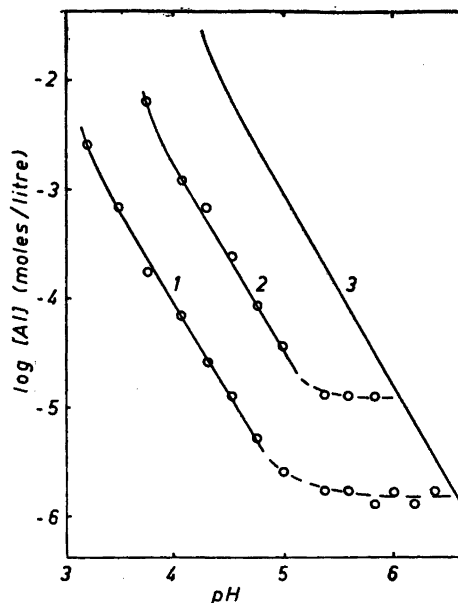


Fig. 10.

Fig. 10. The potassium aluminium sulphate concentrations and corresponding pH values of the substrate when the first signs of interaction between aluminium ions and the rosin acid (Curve 1) and when maximum interaction (Curve 2) is noted. Curve 3 gives the aluminium concentrations and pH values at which aluminium hydroxide precipitates in equilibrium conditions. 20° C. The $KAl(SO_4)_2$ solutions contained 2 moles of sodium chloride and $5 \cdot 10^{-3}$ moles of acetic acid-acetate buffer per litre.

aluminium ions of the substrate and the rosin acid molecules of the monolayer becomes evident in a similar manner. The lowest aluminium ion concentration at which this interaction occurs shifts, however, to lower values with increasing pH. The same applies to the lowest aluminium ion concentration at which the new curve type, the aluminium rosinate type, is fully developed. In all cases this curve type is fully developed at about the same aluminium concentration at which the value of collapse pressure attains its maximum and just before the area per molecule in the monolayer again begins to increase. By means of monolayer studies it thus is possible to determine the end-point of the reaction between aluminium ions and rosin acid which leads to the formation of a uniform monolayer of aluminium rosinate.

The results of the above-mentioned studies on the reaction between rosin acid and aluminium ions are summarized in the diagram of Fig. 10. Curve 1 gives the aluminium concentrations and corresponding pH values at which the interaction begins. Under the conditions to the left of this curve no effect of aluminium ions on the rosin acid monolayer is observed; to the right of the curve the interaction grows in scope until curve 2 is reached. In the conditions given by curve 2 the end point of the reaction is reached. The fully drawn curves give the conditions in which the reaction is independent of the time

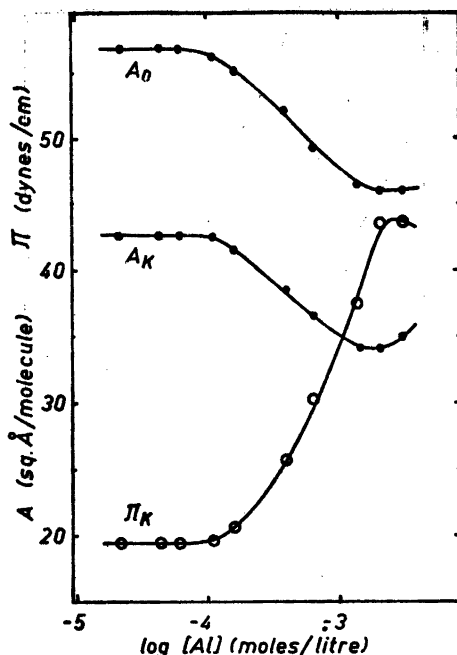


Fig. 11.

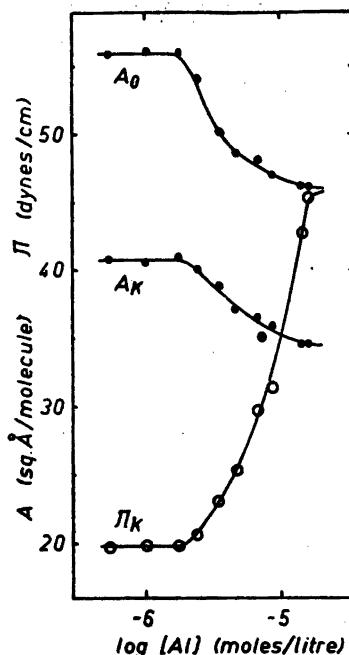


Fig. 12.

Figs. 11–12. The dependence of A_0 , A_K and π_K on the potassium aluminium sulphate concentration at constant pH. 20° C. The substrate contained no added salts.

Fig. 11 pH 4.00, Fig. 12 pH 5.00.

before compression is begun. At low aluminium concentrations, however, the interaction requires some time to attain equilibrium; the dotted parts of 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 rosin acid monolayer, the first signs of an interaction will occur at somewhat lower aluminium ion concentrations and lower pH values. (This phenomenon will be discussed in more detail in a later publication of this series.)

The curve 3 in Fig. 10 gives the pH and aluminium concentration values at which aluminium hydroxide begins to precipitate under equilibrium conditions. This curve is based on investigations of potassium aluminium sulphate solutions of different pH values containing precipitated aluminium hydroxide. After 1–2 days the solution was separated from the precipitate by decantation and analysed for aluminium.

THE INTERACTION BETWEEN ALUMINIUM IONS AND TALL OIL ROSIN ACID MONOLAYERS ON WATER

The conditions promoting interaction between tall oil rosin acid monolayers spread on a substrate containing aluminium ions but no added sodium chloride

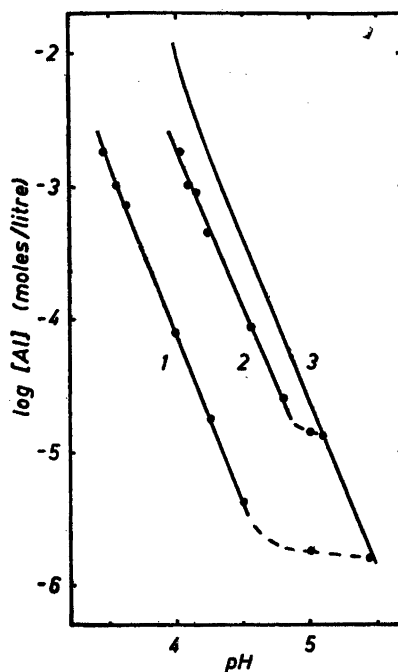


Fig. 13. The potassium aluminium sulphate concentrations and corresponding pH values of the substrate when the first signs of interaction between aluminium ions and the rosin acid (Curve 1) and when maximum interaction (Curve 2) is noted. Curve 3 gives the aluminium concentrations and pH values at which aluminium hydroxide precipitates in equilibrium conditions. 20° C. The $KAl(SO_4)_2$ solutions contained no added salts.

have been studied in a similar manner as above. The ionic strength of the substrate was only *ca.* 0.0001 in these experiments, compared with *ca.* 2.1 in the preceding experiments. The pH was adjusted with dilute HCl or NaOH.

The effect of the aluminium ions on the monolayer becomes evident in changes in the surface pressure-area curves similar to those described above. Figs. 11 and 12 show curves based on the observed changes which refer to the pH values 4.00 and 5.00, respectively.

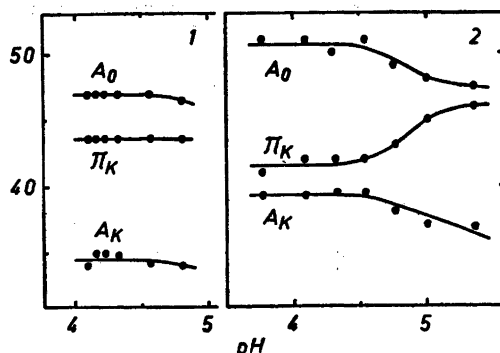


Fig. 14. The values of A_0 , A_K and π_K of dibasic aluminium monorosinate monolayer at different pH values of the substrate. 20° C. 1 The substrate contains no added salts. 2 The substrate contains 2 moles/l sodium chloride and $5 \cdot 10^{-3}$ moles/l acetic acid-acetate buffer.

The experimental results can also in this case be summarized in a similar diagram as in Fig. 10. In this new diagram, Fig. 13, curve 1 shows the pH and aluminium concentration values up to which the properties of an rosin acid monolayer on water remain unchanged, curve 2 shows the conditions in which the end-point of the reaction between the aluminium ions and the rosin acid occurs and an uniform aluminium rosinate monolayer is formed. Curve 3 again gives the conditions where precipitation of aluminium hydroxide occurs. On water, especially when the aluminium concentration is low, the interaction begins and ends at lower pH values than when sodium chloride is present in the substrate. Also the precipitation of aluminium hydroxide takes place at lower aluminium concentrations and pH values. Owing to this, the curve 3 is situated at pH values only 0.2 unit higher than curve 2.

THE PROPERTIES OF THE ALUMINIUM ROSINATE MONOLAYER AT DIFFERENT pH VALUES

It has been possible to determine that when the new curve type, *i.e.* the curve for the aluminium rosinate monolayer, is fully developed, the monolayer is composed solely of dibasic aluminium monorosinate. The evidence proving this will be given in the following paper of this series.

The experimental data given in the preceding sections can be employed to determine how the properties of these aluminium monorosinate monolayers vary with the pH of the substrate (Fig. 14). On water the characteristic properties of the monorosinate monolayer remain unchanged up to a pH of about 4.7, but above this value the area per molecule decreases slowly. On 2 *M* sodium chloride, similar changes occur slightly earlier, at pH 4.5–4.6; also the collapse pressure increases. The data become erratic at pH 4.9 in the former case (water) and at pH 5.5 in the latter case (2 *M* NaCl); in this range the interaction with aluminium ions begins to depend on the time of reaction. Above pH 5.1 and 6.0, in the respective cases, it was not possible to obtain aluminium monorosinate monolayers giving well-defined pressure-area curves.

Table 2. Characteristic data for dibasic aluminium monorosinate monolayers (below pH 4.5).

Substrate	A_0 Å ² per molecule	A_K Å ² per molecule	π_K dynes/cm
Water; pH adjusted with dilute HCl	46.0	34.8	43.6
2 <i>M</i> NaCl, buffered with 5 · 10 ⁻² <i>M</i> acetic acid-acetate	50.7	39.3	41.6

Table 2 gives data which characterize the monolayers of dibasic aluminium monorosinate. These data have been obtained for monolayers formed on substrates with very different aluminium ion concentrations, from 10⁻⁵ *M*

up to 10^{-2} *M*. An increase in the sodium chloride content of the substrate leads to larger areas per molecule of the monolayer substance and causes the collapse pressure to fall slightly.

The deviations from the characteristic values given in Table 2 at higher pH values are observed at the same pH values at which a pure rosin acid monolayer begins to undergo ionization.

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