

Properties of Monolayers of Rosin Acids *

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The properties of monolayers of rosin acids spread on water are relatively little known. A study of *d*-pimaric acid and its hydrogenated derivative tetrahydro-*d*-pimaric acid has been published by Harkins, Ries and Carman¹. Recently Ekwall and Bruun² studied the properties of tall oil rosin acid, a mixture of different rosin acids, in monolayers on substrates of varying pH and of different aluminium ion contents.

From the surface-chemical viewpoint the rosin acids are interesting substances for investigation. The carbon skeleton and the site of the carboxyl group are the same in most of the rosin acids. They differ, however, from each other in the number of double bonds and the location of the latter in the molecule. It is of interest to determine whether the differences in the structures of the rosin acids become evident in the properties of their monolayers. It is only now that this aspect can be closer studied since the methods of purification of the rosin acids have been greatly improved and it is possible to prepare several of the rosin acids in high purity.

The author has studied the properties of the monolayers of abietic acid, dehydro-, dihydro-, and tetrahydroabietic acids and isodextropimaric acid.

EXPERIMENTAL

The monolayers were investigated with a recording surface balance of the Wilhelmy-Dervichian type as improved by Andersson-Groth, Ställberg-Stenhagen and Stenhagen³. The monolayer was compressed at a rate of 5 cm per minute and the compression was commenced two minutes after the spreading of the substance under study. The rosin acids were added to the surface of the substrate in a benzene solution (concentration $2 \cdot 10^{18}$ molecules per millilitre) with an "Aglä" micrometer syringe.

* Preliminary communication read at the VII Nordiska Kemistmötet in Helsingfors 1950. Abstract in the Proceedings of the Meeting, Helsingfors 1951, p. 164 and in *Teknisk Tidskrift* **80** (1950) 790.

The twice distilled water used in the experiments had a specific conductance of approximately $0.6 \cdot 10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. The required pH was obtained by adding hydrochloric acid. When studying the influence of the pH of the substrate on the monolayers, the substrate was first brought to pH 3.8, and then the pH was increased by successive additions of sodium hydroxide. The pH measurements were carried out on aliquots of the aqueous solution with a electronic potentiometer (Radiometer Type PHM 3), fitted with a glass electrode and a saturated calomel reference electrode. In order to avoid oxidation in the case of abietic acid, the surface balance measurements with this acid were conducted in a nitrogen atmosphere. The substrate was saturated with nitrogen and contained 10–15 mg hydroquinone (Merck, pro analysi) per litre.

The rosin acids studied were obtained from the Research Laboratory of the Hercules Powder Company, Wilmington, Delaware. According to information received from Dr. G. C. Harris of that laboratory the abietic acid and dehydroabietic acid were pure and free from isomeric acids. The dihydro- and tetrahydroabietic acids were prepared by partial and complete hydrogenation of abietic acid. The resulting products were mixtures of isomeric acids, but were otherwise pure. Isodextropimaric acid was prepared according to the method described by Harris and Sandermann⁴.

Owing to its tendency to oxidize easily, the abietic acid was stored in a closed evacuated glass tube. The preparation was recrystallized immediately before use from acetone to which 1 g hydroquinone per litre had been added. Another sample of pure abietic acid in the form of its butylamine salt was obtained from the Svenska Träforskningsinstitutet, Stockholm. The abietic acid was liberated from its salt with boric acid, shaken with ether and recrystallized as described immediately before use.

The corrected melting points of the rosin acids and their specific rotations in absolute alcohol were:

Abietic acid (both samples)	m. p. 170.2–172.7° C,	$[\alpha]_D^{20} = -103^\circ \text{ to } -104^\circ$;
dehydroabietic acid	m. p. 173.3–174.8° C,	$[\alpha]_D^{20} = +65^\circ \text{ to } +67.5^\circ$;
dihydroabietic acid	m. p. 133.8–136.8° C,	$[\alpha]_D^{20} = +17^\circ \text{ to } +21^\circ$;
tetrahydroabietic acid	m. p. 149.4–152.4° C,	$[\alpha]_D^{20} = +9^\circ \text{ to } +13^\circ$;
isodextropimaric acid	m. p. 162.9–164.9° C,	$[\alpha]_D^{20} = 0^\circ$.

RESULTS

The pressure-area curves of the pure rosin acid monolayers

a. *Experiments at pH 3.0.* Fig. 1 shows the pressure-area curves for tetrahydroabietic acid (TAbH), dihydroabietic acid (DiAbH), abietic acid (AbH), isodextropimaric acid (IdPH) and dehydroabietic acid (DeAbH) monolayers on water with a pH of 3.0 at 20° C ($\pm 0.3^\circ$). Certain characteristic data obtained from these pressure-area curves are collected in Table 1. The values given are average values from six curves recorded in succession for each acid. The different values for A_K and A_{15} deviated less than $\pm 0.2 \text{ sq.}$

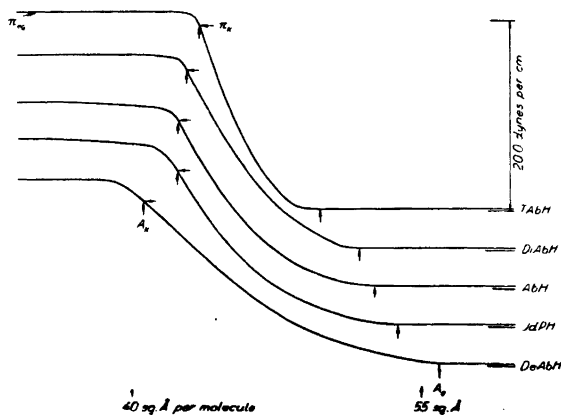


Fig. 1. Pressure-area curves for monolayers of tetrahydroabietic (TAbH), dihydroabietic (DiAbH), abietic (AbH), isodextropimaric (IdPH) and dehydroabietic (DeAbH) acids. Aqueous substrate containing hydrochloric acid ($\text{pH} = 3.0$).

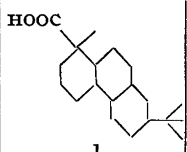
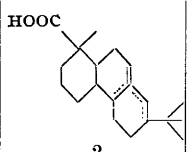
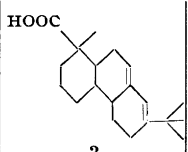
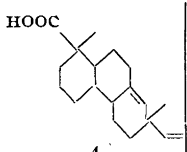
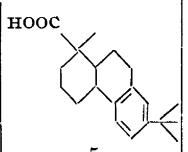
Å from the average. In the table the acids are listed in the order of their degree of unsaturation as indicated by the schematic structural formulae. The skeleton of isodextropimaric acid differs somewhat from those of the abietic acids, but has been included for comparison.

From Fig. 1 it is seen that the pressure-area curves for the different rosin acids are very similar. Both the areas per molecule and the collapse pressures of the monolayers of these acids are approximately the same for the acids investigated. Compression of the monolayers occurs between the molecular areas 56 and 40 sq.Å, while the surface pressures at which the films collapse (π_K) are within the range 16 to 20 dynes per centimetre. The acids form liquid layers on compression. The properties of the rosin acids studied resemble greatly those of *d*-pimaric acid and tetrahydro-*d*-pimaric acid described by Harkins *et al.*¹, when the differences in method of study and temperature are taken into account.

A closer inspection of the values of Table 1, however, reveals certain gradual differences between the rosin acids investigated. Both A_K and A_{15} decrease in value in the order TAbH, DiAbH, AbH, IdPH, DeAbH. The difference in the values of A_K for TAbH and DeAbH is 3.0 sq.Å. The corresponding difference for A_{15} is 2.3 sq.Å and for π_K about 2.2 dynes per cm (excluding IDP). A_0 , however, undergoes an increase of 6–7 sq.Å in the order of acids given.

The gradual changes noted in the case of A and π appear to be connected with the structures of the rosin acid molecules, particularly with the number of double bonds. It is clearly evident that the TAbH molecules which do not

Table 1. Data relating to the pressure-area curves for rosin acid monolayers shown in Fig. 1.

Rosin acid		1 Tetra- hydro- abietic acid TAbH	2 Dihydro- abietic acid DiAbH	3 Abietic acid AbH	4 Iso- dextro- pimaric acid IdPH	5 Dehydro- abietic acid DeAbH
Area at the collapse point of the monolayer (sq.Å per molecule)	A_K	43.4	42.9	42.0	42.6	40.4
Area when the surface pressure is 15 dynes per cm	A_{15}	44.2	43.9	42.8	42.8	41.9
Area when the first increase in pressure is observed	A_0	49.6	51.9	52.2	54.1	55.9
Surface pressure at the collapse point of the monolayer (dynes per cm)	π_K	19.5	19.2	17.9	15.8	17.3
Surface pressure when equilibrium pressure is attained after the collapse of the monolayer	$\pi_{K_{eq}}$	20.8	20.3	19.5	19.7	19.6
Compressibility of the monolayer just before collapse $K = -\frac{\delta A}{\delta \pi} \cdot \frac{1}{A}$	K	0.0041	0.0058	0.0066	0.0077	0.013
Schematic structural formulae						

contain double bonds in their ring system take up the largest area in the compressed monolayer. With increase in the number of double bonds A_K decreases in the series DiAbH, AbH, IdPH, DeAbH, the latter occupying the smallest area. It is also seen that the double bonds increase the affinity of the molecules for water. The larger the number of double bonds, the earlier

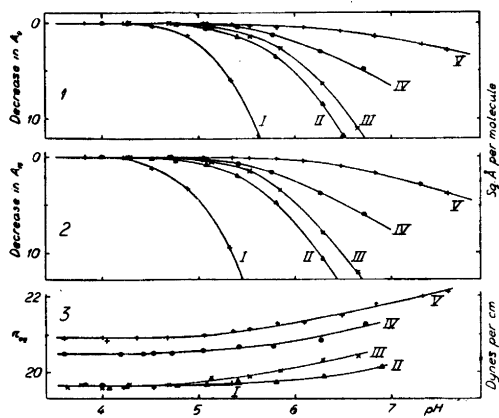


Fig. 2. The values of $\pi_{K_{eq}}$ (diagram 3) and the decrease in the values of A_0 (d. 1) and A_{15} (d. 2) observed in the pressure-area curves for various rosin acids at increasing pH values of the substrate at 20° C. I DeAbH, II AbH, III IdPH, IV DiAbH, V TAbH.

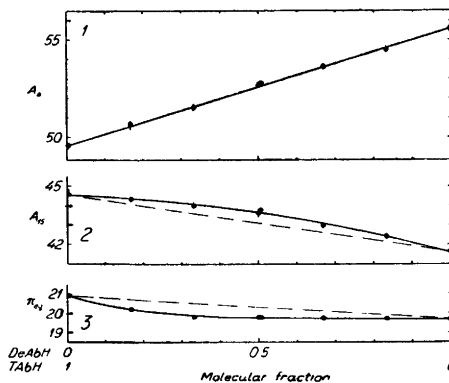


Fig. 3. The values of A_0 (1), A_{15} (2), and $\pi_{K_{eq}}$ (3) from the pressure-area curves of monolayers containing TAbH and DeAbH. pH = 3.0 20° C.

the surface pressure begins to increase on compression and the higher the value of A_0 . This value is largest in the case of DeAbH and smallest for TAbH.

The values of most of the properties of the monolayer of IdPH with two double bonds, one of these in the side chain, lie between those of DeAbH and AbH. The monolayer of IdPH shows, however, the lowest π_K value of all these acids.

b. *Experiments at varying pH.* Pressure-area curves were also recorded for the monolayers of the rosin acids mentioned above on substrates of different pH values (2 to 8) to determine to what extent the dependence of the properties of the monolayers on the pH value of the underlying water is determined by the molecular structure.

Fig 2 illustrates the relation between the pH of the substrate and the quantities A_0 , A_{15} and $\pi_{K_{eq}}$ (Table 1). These quantities remain unaltered up to pH 4.2; above this value the areas taken up by the rosin acids begin to decrease, first that of DeAbH, followed by AbH, IdPH, DiAbH and THAB. $\pi_{K_{eq}}$ undergoes an increase with increasing pH. This increase is smallest for DeAbH.

The decrease in area with increasing pH of the substrate coincides with the beginning of ionization in the rosin acid monolayer and with the accompanying increase in the solubility of the monolayer substance. This solubility is highest in the case of DeAbH and AbH and is weakest with TAbH.

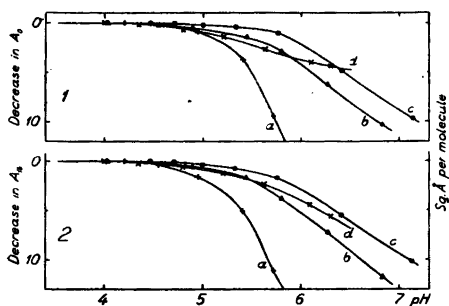


Fig. 4. The decrease in the values of A_0 (1) and A_{15} (2) in the pressure-area curves of binary rosin acid mixtures with increasing pH of the substrate. Molar ratio of components 1 : 1. 20° C. a) TAbH + DeAbH; b) TAbH + AbH; c) TAbH + IdPH; d) DiAbH + IdPH.

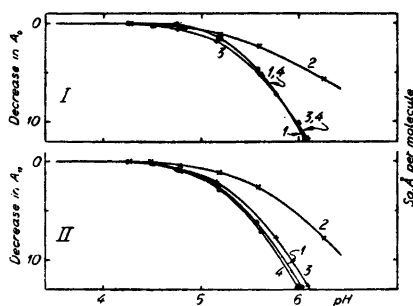


Fig. 5. The decrease in the values of A_0 (I) and A_{15} (II) in the pressure-area curves of monolayers of a purified Finnish tall oil rosin and of certain ternary rosin acid mixtures with increasing pH. 20° C. 1 (●) tall oil rosin, 2 (x) AbH 50 %, IdPH 25 %, DiAbH 25 %, 3 (+) AbH 50 %, IdPH 25 %, DeAbH 25 %, 4 (Δ) AbH 33 1/3 %, IdPH 33 1/3 %, DeAbH 33 1/3 %.

The differences in the structures of rosin acids are clearly evident also in the properties of the monolayers at different acidities of the substrate.

Monolayers of binary rosin acid mixtures

A number of binary mixtures of the rosin acids were studied to determine whether the components affect each other's properties in the mixed monolayer or whether the individual properties of the component acids become evident in the mixtures.

a. *Experiments at pH 3.0.* Fig. 3 shows the variation of A_0 , A_{15} and π_{Keq} for monolayers containing TAbH and DeAbH at pH 3.8. On the left side are given the values for the pure TAbH layer and on the right those for the pure DeAbH layer. Each point in the curves is an average value from 4 to 5 successive measurements which fall within the range indicated. A_0 is seen to vary linearly with the ratio of the components in the layer. Also A_{15} varies in a similar manner but the values of A_{15} are higher than would have been expected. The molecules thus appear to take up larger areas in the mixed monolayers than in the simple monolayers. This is accompanied by a decreased strength of the monolayer as shown by the values for the surface pressures π_{Keq} given by the lowest curve in Fig. 3.

b. *Substrates of different pH.* Four binary rosin acid mixtures were studied with varying pH values of the substrate, *viz.*, TAbH + DeAbH (Fig. 4, curves a), TAbH + AbH (curves b), TAbH + IdPH (curves c) and DiAbH + IdPH (curves d). In all cases the mole ratio of the components was unity. Marked differences are noted between the properties of the mixed monolayers. A comparison of curves for the mixtures and the single acids (Fig. 2) shows that the components behave to a large degree independently of each other; the curves of Fig. 4 correspond to curves calculated for the mixtures from the curves of the pure components given in Fig. 2.

Tall oil rosin acid

According to Sandermann⁵ purified tall oil rosin acid contains approximately 50 per cent abietic acid, 25 per cent dextropimaric acid and 25 per cent dehydro-, dihydro-, and tetrahydroabietic acids. According to Harva⁶ purified Finnish tall oil rosin contains 30 to 40 per cent abietic acid. The compositions of tall oil rosin acids vary, however, considerably owing to various factors. For special uses, *e.g.*, in the paper industry, a method for defining tall oil rosin acid is of importance. An attempt has been made to determine whether the surface balance can be employed to indicate variations in the composition of the tall oil rosin.

The properties of the monolayer of a purified Finnish tall oil rosin ($[\alpha]_D^{20} = -44$ to -45° in absolute alcohol) are shown in Fig. 5, curves 1.⁷ Curves 2 apply to a rosin acid mixture containing 50 % AbH, 25 % IdPH, 25 % DiAbH, curves 3 to a mixture containing 50 % AbH, 25 % IdPH, 25 % DeAbH, and curves 4 to a mixture containing 33 1/3 % AbH, 33 1/3 % IdPH, and 33 1/3 % DeAbH. The latter curves (4) correspond fairly well with those obtained for the purified tall oil rosin (1). Curves 3 relating to a mixture containing more AbH and less DeAbH are seen to differ clearly from the former curves (4). Substitution of DeAbH for DiAbH in the mixtures represented by curves 3 leads to different values of A_0 and A_{15} as shown by curves 2. It is hardly possible to prepare a mixture containing known rosin acids that would exactly correspond to tall oil rosin in its monolayer properties. It seems, however, that with the surface balance it is possible to differentiate between various tall oil rosins and other rosin acid mixtures.

SUMMARY

The monolayers of abietic, dehydro-, dihydro- and tetrahydroabietic acids have been studied with a surface balance. The pressure-area curves of the monolayers are of the same form. The areas per molecule and the collapse

pressures of the monolayers show differences. These differences appear to be connected with the structure of the rosin acid molecules, particularly with the number of double bonds in the molecules.

The properties of the rosin acid monolayers on substrates of different acidities have also been studied. The beginning of the ionization of the rosin acids with accompanying increase in the solubility of the monolayer substance is seen from the increase in the collapse pressure and from the decrease in the area per molecule. Differences are noted also in this respect between the various rosin acids.

The properties of isodextropimaric acid resemble most closely those of abietic acid. The pressure-area curve of the monolayer shows a lower collapse pressure than the curves for the acids of the abietic series.

A study of binary mixtures of rosin acids indicated that in most cases the individual monolayer properties of the components become evident in the properties of the mixed monolayers.

An investigation of ternary rosin acid mixtures and of a Finnish tall oil rosin showed that the surface balance can be employed to indicate differences in composition of rosin acid mixtures.

This work is connected with studies of the theory of paper sizing with rosin which are being conducted at the Institute of Physical Chemistry of Åbo Akademi in collaboration with *Ab Centrallaboratorium* of Helsingfors.

I am indebted to Professor Per Ekwall, the Head of the Institute, for helpful discussions and for the opportunity of using the facilities of the Institute.

I wish to thank Dr. C. G. Harris of the Hercules Powder Company for the pure rosin acids which he has put at the disposal of the Institute and to Mr. E. Back, Civ. E., of the Svenska Träforskningsinstitutet for the sample of butylamine abietate.

This work has been supported by a state grant.

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Received November 8, 1951.