An Interpretation of the Effect of Ionization upon Monolayer Properties of Rosin Acids

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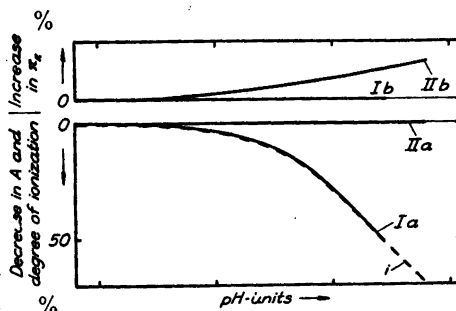*Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland*

Fig. 1. *The expected effect of ionization of a monolayer substance upon its monolayer properties on an aqueous substrate with a low electrolyte concentration when the molecules are* I *weakly hydrophobic,* II *strongly hydrophobic. C u r v e a: Decrease in the surface area A of the compressed monolayer, b: Increase in the monolayer collapse pressure* π_K*. The dotted line i gives the variation of the degree of ionization.*

When the molecules in a monolayer undergo ionization their hydrophilic properties become stronger. It may be expected that this strengthening of the hydrophilic properties will affect the monolayer properties in a different manner depending on how strongly hydrophobic the molecules are. On aqueous substrates of low electrolyte concentration the following relationship may be expected to apply between the hydrophobic properties of the molecules and the properties, *e. g.* the stability and surface area, of the monolayers they form. In the case of weakly hydrophobic molecules in which the hydrophilic properties predominate after ionization it will be expected that the ionized molecules will not remain in the monolayer when it is compressed. If it is assumed that an equilibrium represented by the equation

$$\frac{[H_3O^+] \cdot A^-}{HA} = K$$ applies to the ionization

of an acid HA in the monolayer and that the ionized molecules do not remain in the monolayer on compression, it is to be expected that the curve Ia in Fig. 1 representing the decrease in the area A taken up by the spread substance with increasing pH of the substrate will be similar to the curve i in the same figure showing the variation of the degree of ionization, *i. e.* the ratio of ionized molecules (A^-) to the total number of molecules $(HA + A^-)$ as a function of the pH of the substrate. When the ionized molecules do not remain in the monolayer, the stability of the monolayer as indicated by the collapse pressure π_K will not undergo change. The pressure π_K will hence remain constant

with increasing degree of ionization, Fig. 1, curve Ib.

In the other case in which the hydrophobic properties predominate even in spite of the ionization, the ionized molecules will be held in the monolayer even when it is compressed. The monolayer properties can be expected to vary in the following manner. The area A will not be altered with increasing ionization, Fig. 1, IIa. Factors such as changes in the tilt of the molecules in the surface layer and changes in the interaction between the molecules may, however, to some extent cause variations in A. The ionized molecules will be more strongly anchored in the surface of the substrate than the unionized molecules and this will result in higher values of π_K with increasing ionization, Fig. 1, IIb.

These two possibilities correspond to limiting conditions. If there exists a suitable balance between the hydrophobic and hydrophilic properties it will be expected that the curve representing the decrease in A will lie between the two curves *Ia* and *IIa*. π_K will increase to some extent, but will be smaller than in case IIb.
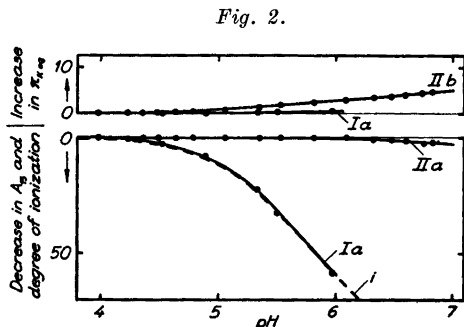
11

Fig. 2.

Fig. 2—3. The effect of ionization upon the properties of rosin acid monolayers. F i g. 2. I dehydroabietic, II tetrahydroabietic acid. F i g. 3. I abietic, II dihydroabietic acid. C u r v e s a: Decrease in the area A_{15}, b: Increase in the collapse pressure π_{Keq}. Curve i give the variation of the degree of ionization. 20° C. The pH of the aqueous substrate has been reduced first to pH 3.8 by adding hydrochloric acid, and then increased by adding sodium hydroxide solution.

Fig. 3.
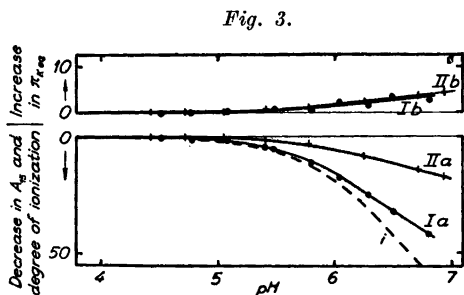
On the basis of the foregoing, if the strength of the hydrophobic properties of the molecules determines the effect of ionization upon the properties of the compressed monolayer, it is to be expected that in the case of molecules with weakly hydrophobic properties only the area A will undergo a change, and in the case of strongly hydrophobic molecules only the pressure π_K will be altered. In the case of molecules with intermediate hydrophobic properties in which there exists a balance between the hydrophobic and hydrophilic properties in the ionized state, both A and π_K will be affected.

In the rosin acid series, dehydroabietic, abietic, dihydroabietic, and tetrahydroabietic acid, the hydrophobic character of the molecules increases with decreasing number of double bonds in the molecule. The effect of ionization upon the monolayer properties of these acids on substrates with very low electrolyte concentrations is recently investigated [1] and is shown in Figs. 2—3. The curves for dehydroabietic acid, Fig. 2, I, indicate a marked decrease in A_{15} (the area at a surface pressure of 15 dynes per cm) and practically unaltered π_{Keq} (the equilibrium pressure after the collapse of the monolayer). The curve A_{15} almost exactly corresponds to the curve i for the degree of ionization calculated taking for K the value $10^{-5.84}$. At pH 5.97, a decrease in A_{15} of 58 per cent is accompanied by an increase in π_{Keq} of only 0.6 per cent. The effect of the ionization on the dehydroabietic acid monolayer thus corresponds very well with the curves I in Fig. 1, which were drawn for the case of weak hydrophobic properties of the molecule. The curves for tetrahydroabietic acid, Fig. 2, II, resemble the curves II in Fig. 1, which apply to strong hydrophobic properties of the monolayer substance. The increase in π_{Keq} is marked (5 per cent at pH 7.0), whereas the decrease in A_{15} is relatively insignificiant (3—4 per cent). Fig. 3, I, for abietic acid and Fig. 3, II, for dihydroabietic acid indicate marked changes in both π_{Keq} and A_{15}. The increase in π_{Keq} is about 3 per cent for abietic acid at pH 6.81, the decrease in A_{15} 41.2 per cent. The corresponding percentages for dihydroabietic acid are 4 per cent and 17 per cent at pH 6.94. Abietic and dihydroabietic acids thus occupy an intermediate position with respect to the effect of ionization on the monolayer properties, which is to be expected since with respect to their hydrophobic properties they are situated between dehydroabietic and tetrahydroabietic acid.

The behavior of the rosin acids shows

clearly that the effect of ionization upon the monolayer properties is connected with their hydrophobic character. It is also evident that the strength of the hydrophobic properties largely determines the nature of the effect. Differences similar to those noted for the rosin acids may also be found among other groups of substances in which the hydrophobic properties undergo similar variations.

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1. Bruun, H. *Acta Chem. Scand.* **6** (1952) 494.

Thiohydrazides and Thiohydrazones: A New Class of Antibacterial Substances

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In 1934 Jensen [1] prepared several co-ordination compounds of thiosemicarbazide and substituted thiosemicarbazides. Recently Jensen and Miquel [2] found that thiobenzhydrazide, $C_6H_5CSNHNH_2$, forms nickel complexes of the same type as are formed by the thiosemicarbazides. A close parallel appears to exist between tuberculostatic activity of the thiosemicarbazones and their ability to form co-ordination compounds with copper [3]. Since the complex compounds of thiosemicarbazides and thiohydrazides are similar we should expect that thiohydrazones would also possess antibacterial activity. A large number of thiohydrazides and thiohydrazones were therefore prepared and tested. Preliminary experiments showed that both classes of compounds were antibacterial as well as fungistatic, so we are now making a more detailed investigation of their activity.

The thiohydrazides were prepared by reaction of esters of dithioacids or the free dithioacids with hydrazine. The following new thiohydrazides were prepared:

Thiophenylacethydrazide. M.p. 71°.

$C_8H_{10}N_2S$ (166.2)
Calc. C 57.82 H 6.07 N 16.86 S 19.26
Found » 57.52 » 5.95 » 16.96 » 19.25

2-Hydroxythiobenzhydrazide. M.p. 102°.

$C_7H_8ON_2S$ (168.2)
Calc. C 50.00 H 4.80 N 16.66 S 19.07
Found » 49.98 » 4.85 » 16.95 » 18.92

4-Hydroxythiobenzhydrazide. M.p. 208°.

$C_7H_8ON_2S$ (168.2)
Calc. C 50.00 H 4.80 N 16.66
Found » 50.25 » 4.73 » 16.83

4-Methoxythiobenzhydrazide. M.p. 126°.

$C_8H_{10}ON_2S$ (182.2)
Calc. C 52.72 H 5.53 N 15.38 S 17.59
Found » 52.85 » 5.48 » 15.31 » 17.30

3-Methoxy-4-hydroxythiobenzhydrazide.

M.p. 148°.

$C_8H_{10}O_2N_2S$ (198.2)
Calc. C 48.48 H 5.09 N 14.14
Found » 48.68 » 5.18 » 14.06

4-Acetamidothiobenzhydrazide. M.p. 234°.

$C_9H_{11}ON_3S$ (209.3)
Calc. C 51.67 H 5.30 N 20.09
Found » 51.71 » 5.38 » 20.41

4-Dimethylaminothiobenzhydrazide.

M.p. 170°.

$C_9H_{13}N_3S$ (195.3)
Calc. C 55.37 H 6.71 N 21.53
Found » 55.31 » 6.75 » 21.50

2-Furanethiocarboxhydrazide. M.p. 135°.

$C_5H_6ON_2S$ (142.2)
Calc. C 42.25 H 4.26 N 19.71 S 22.52
Found » 42.28 » 4.44 » 19.92 » 22.45