

## Infrared Spectra and Surface Pressure of Myristic Acid Monolayers on Iron Chloride Solutions

HERMANN MÜLLER, STIG FRIBERG

*The Laboratory for Surface Chemistry, Royal Swedish Academy of Engineering Sciences,  
Stockholm, Sweden*

and HENRIK H. BRUUN

*Institute of Wood Chemistry, Abo Academy, Abo, Finland*

The surface pressure of monolayers of myristic acid on substrates containing  $10^{-3}$  M FeCl<sub>3</sub> was registered at different pH values. The monolayers were compressed to the solid state, collected as a monolayer on a KRS-5 crystal and the infrared spectra of the layers were recorded. These spectra show that the carboxyl groups are ionized at pH values above 2.30 and that the hydrocarbon parts of the acids are in a crystalline state when collected. This crystallinity disappears when the carboxyl group is ionized.

Since Bruun<sup>1</sup> made his pioneering research on the infrared spectra of collected monolayers of rosin acids on substrates containing aluminium salts, modifications of this technique has been used for investigations on reactions between acids and different carboxylic acid monolayers. Ellis and Pauli<sup>2</sup> investigated monolayers collected with the Blodgett technique<sup>3</sup> to a multilayer on an AgCl crystal. They believed that the reaction between aluminium ions and stearic acid led to the formation of *tri*-soaps in the monolayer. This opinion was rejected by Friberg and Bruun, who found the formation of monosoaps in monolayers of tetrahydroabiatic acid on aluminium salt solutions,<sup>4</sup> and *mono*-soaps also at the interphase layer between a solution of stearic acid in carbon tetrachloride and an aqueous solution of aluminium chloride.<sup>5</sup>

Bruun and Friberg made an investigation of tetrahydroabiatic acid on ferric salt solutions<sup>6</sup> by means of monolayers collected, dried and pressed in KBr pellets. They found signs of soap formation at pH values below those where the formation of iron hydroxide takes place. The percentage of the carboxyl groups which were ionized was found to be roughly proportional to the amount of iron which had formed complexes  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_x]^{2+}$ .

The present investigation was undertaken in order to elucidate the possibilities of using monolayers collected on KRS-5 crystals for studies of this kind. It was believed that a single monolayer would be sufficient to give identifiable spectra and that the problems connected with the co-collected water, the drying and pressing procedure would then be non-existent.

### EXPERIMENTAL

*Instruments.* The pressure area curves were made by a self-recording surface balance of Langmuir type, modified according to Ställberg-Stenhagen, Stenhagen and Andersson.<sup>7</sup>

Infrared spectra were recorded on a Perkin-Elmer 337 Grating infrared spectrophotometer. The cell TR-9 (RJJC) uses six internal reflections of the radiation, which equals twelve layers in transmission studies.

pH measurements were made on a Radiometer PHM 4C with a glass electrode and a calomel electrode, which were always calibrated with pH buffer before measuring.

*Surface pressure.* The myristic acid, prepared at the Institute of Biochemistry, Gothenburg, with a purity of more than 99.5 %, was dissolved to  $9.6 \times 10^{17}$  molecules per ml in redistilled petroleum ether (60–80°C). 0.1 ml of this solution was spread on the subphase surface. The monolayer was compressed 15 min later at a speed of 80 cm<sup>2</sup>/min and the pressure was recorded. The subphase consisted of a  $10^{-3}$  M FeCl<sub>3</sub>-solution prepared from FeCl<sub>3</sub> (Merck *p.a.*) and redistilled water. The pH was adjusted by adding NaOH or HCl, both of *p.a.* quality. Since the solutions pH > 2.3 are not in equilibrium, the pH values of these solutions were controlled at 24 h intervals, and a moderate criterium of equilibrium was considered acceptable when the pH value did not change to a measurable degree between these determinations.

The trough and other glassmaterial for these experiments were carefully cleaned and were kept in as dustless conditions as possible. Before the investigations the subphase surface was cleaned in the usual manner.

*Infrared spectra.* A monolayer was spread on the subphase and compressed 15 min later to the solid state. The monolayer formed was collected on a crystal of thallium iodide bromide (KRS-5) for the IR investigation by dipping the crystal in the trough through the monolayer, and the IR spectrum then recorded (Fig. 1). Parts of the spectra were enlarged by means of a Perkin-Elmer Scale Expansion Recorder 159.

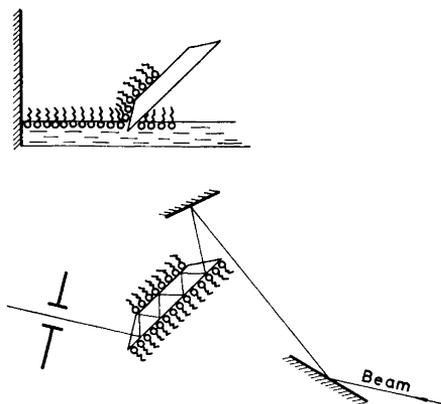


Fig. 1. The monolayer is collected on the crystal at high pressure and the spectrum recorded after multiple internal reflection.

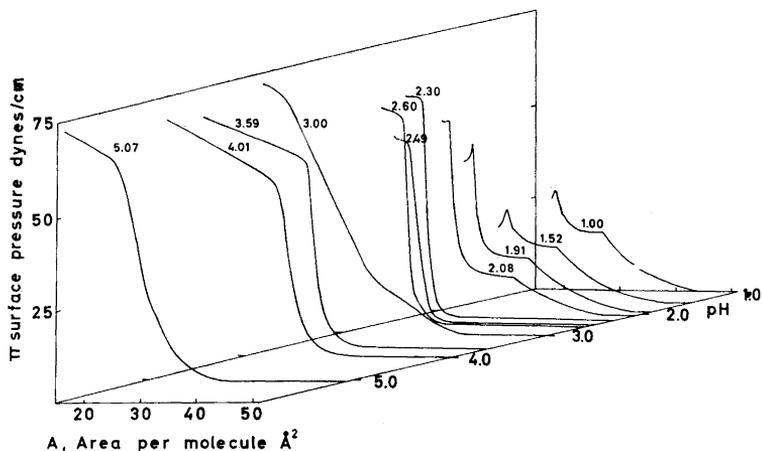


Fig. 2. The pressure-area curves of myristic acid monolayers on iron chloride solutions ( $10^{-3}$  M) at different pH values.

### RESULTS

*Surface pressure.* The surface pressure *versus* the molecular area (Fig. 2) shows the behaviour of a carboxylic acid, when spread on the solution of low pH values. The changes between the regions liquid-expanded, liquid-condensed, and also to the solid state is apparent immediately before the collapse. At pH values above 1.5 but below 2.30 the liquid-expanded state is reduced and the solid state increases considerably. At pH values of 2.30 and above, the liquid state has disappeared and the layer passes through a very short transformation region into the solid state. At higher pH values, the curves have very limited value, due to the problem of obtaining equilibrium in a reasonable time, and also to increased solubility of the monolayer. No comments will be made on these curves here.

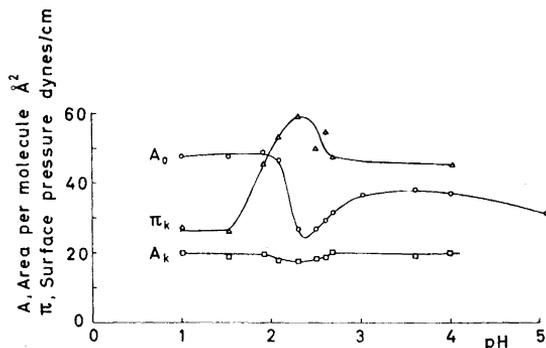


Fig. 3. The area  $A_0$  (first signs of increasing pressure),  $A_k$  (the collapse point) and  $\pi_k$  (the collapse pressure) as functions of the pH value.

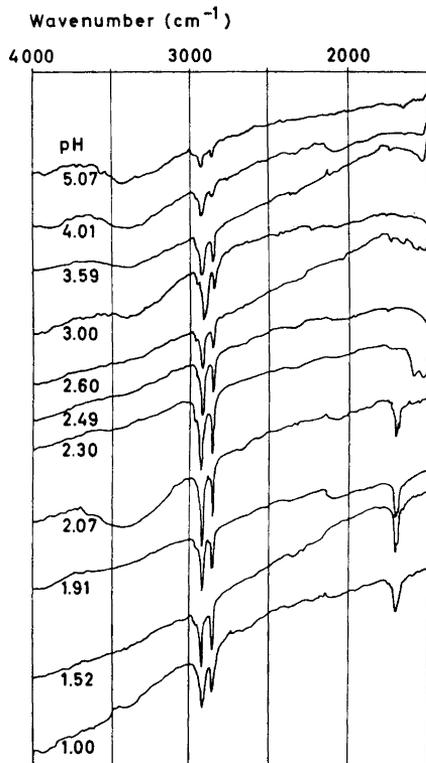


Fig. 4. Part of the infrared spectra of the collected monolayers.

The area,  $A_0$ , where the first signs of increasing pressures are shown, the area  $A_k$  at the collapse point and the collapse pressure functions of the pH value are presented in Fig. 3. These values show the reduction in  $A_0$  and  $A_k$  and the increase of  $\pi_k$  at the pH of precipitation of iron hydroxide in general agreement with earlier investigations.<sup>6,8</sup>

*Infrared spectra.* The transmittance in the region 4000–1500  $\text{cm}^{-1}$  at different pH values is presented in Fig. 4. Detectable amounts of hydrogen bonded OH groups are found at the pH values 2.07 and above 3.00, which is shown by the appearance of the very broad band centered about 3400  $\text{cm}^{-1}$ .

The absorption of the carboxyl group changes with the pH value, which is easily observed in Fig. 5, where a small region is shown of the spectra 1800–1500  $\text{cm}^{-1}$  magnified about ten times. This figure shows how the absorption is split into two badly resolved parts with wave numbers slightly above and below 1700  $\text{cm}^{-1}$ . The part with the wave number below 1700  $\text{cm}^{-1}$  increases with increasing pH value up to 2.07. At pH 2.30 these bands have disappeared completely and two new bands at 1600 and 1550  $\text{cm}^{-1}$  appear. At higher pH values the intensity of the bands changes, but the main trend is an increasing intensity of the band with the lowest wave number.

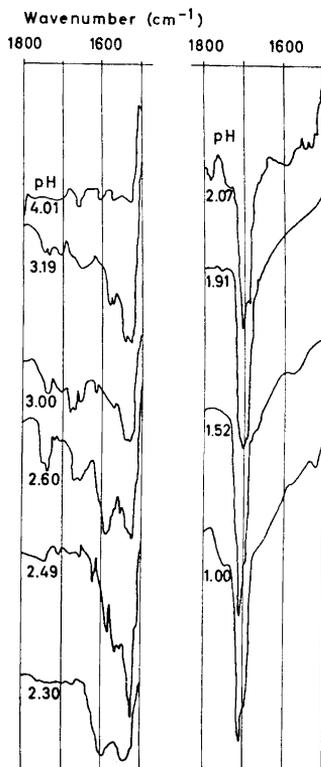


Fig. 5. Infrared transmittance of the carboxyl group at different pH values.

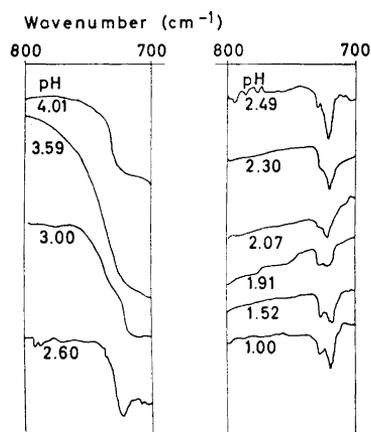


Fig. 6. Infrared absorption of the rocking vibration of the methylene groups.

The infrared spectra gave surprising information on the state of the hydrocarbon part of the monolayers. The transmittance in the region  $800\text{--}700\text{ cm}^{-1}$  is shown in Fig. 6. The peak at  $720\text{ cm}^{-1}$  is split into two bands at pH values lower than 2.30, a split which has not completely disappeared before the pH value reaches 2.60. The splitting of this absorption is characteristic of hydrocarbon chains in a crystalline state.

#### DISCUSSION

The results have given ample evidence that the changes in the curves of surface pressure plotted against molecular area at pH 2.30 are due to the ionization of the carboxyl groups in the monolayer in the reaction with the iron ions in the solution. These results are quite in accordance with those from earlier investigations by Bruun and Friberg<sup>6</sup> on tetrahydroabietic acid monolayers. The present results show, however, no soap formation at pH

values below 2.30 which was observable in the earlier spectra. The reason for this is not completely clarified but will be treated in a separate investigation about the influence of different techniques on the results.

It should be noted that the absorption of the carboxyl group of the acid is not completely unchanged at pH values below pH 2.30. The absorption is split into two peaks, of which the low frequency increases with the pH value. This is assumed to be due to hydroxo-complexes of iron present in the solution (Fig. 7), which are supposed to form rather strong hydrogen bonds

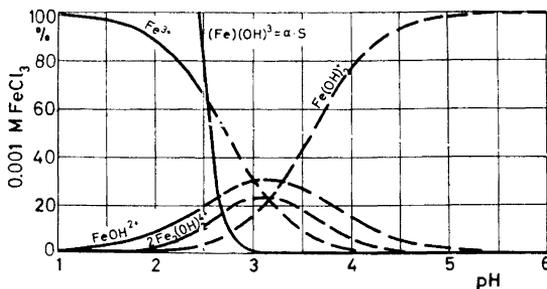


Fig. 7. Different iron hydroxo-complexes present in a solution of iron chloride ( $10^{-3}$  M).<sup>6</sup>

with the carboxyl groups in the monolayer. This behaviour was earlier believed to be due to dipole-induced dipole interaction, but is given a more plausible explanation when these hydroxo-complexes are concerned. This opinion is supported by the rather strong absorption at  $3400\text{ cm}^{-1}$ , which is detectable in the spectrum of the monolayer when the substrate has a pH value of 2.07.

The spectra contain no detectable or very weak absorptions due to OH groups at pH values above 2.30 and below 3.00. This can, however, not be taken as a proof of the formation of iron *tri*-soaps in the monolayer. The hydroxide groups can be hydrogen bonded to the carboxyl group with very strong bonds, which absorb at very low wave numbers.<sup>9</sup>

The rather strong absorption due to hydroxide groups which appears at pH values above 3 are explained by the presence of iron hydroxide in the monolayer. This supports the proposal of Bruun and Friberg<sup>6</sup> on the formation of layers of iron hydroxide attached to and beneath the monolayer.

In the present results no absorption due to the carboxyl group at  $1715\text{ cm}^{-1}$  can be observed at pH values above 2.3, which is not in accordance with our earlier results on the monolayers of tetrahydroabiatic acid.<sup>6</sup> This difference cannot be explained yet, but possibly some information will appear concerning this phenomenon in a future investigation on the influence of the results of different  $pK_a$  values of the acids and different methods of preparation.

The signs of crystallinity of the hydrocarbon parts of the molecules are very interesting. This behaviour has not been observed before on layers collected as monolayers and possibly presents new possibilities in the investigations of monolayers by means of infrared spectroscopy.

## REFERENCES

1. Bruun, H. H. *Acta Chem. Scand.* **9** (1955) 1721.
2. Ellis, J. W. and Pauli, J. L. *J. Colloid. Sci.* **19** (1964) 755.
3. Blodgett, K. J. *J. Am. Chem. Soc.* **57** (1935) 1007.
4. Friberg, S. and Bruun, H. H. *Arkiv Kemi* **25** (1966) 491.
5. Friberg, S. *Arkiv Kemi* **25** (1966) 533.
6. Bruun, H. H. and Friberg, S. *TAPPI*.
7. Andersson-Groth, K. J. I., Ställberg-Stenhagen, S. and Stenhagen, E. In *The Swedberg 1884 30/8 1944*. Uppsala 1944, p. 11.
8. Spink, J. A. and Sanders, J. V. *Trans. Faraday Soc.* **51** (1955) 1154.
9. Hadzi, D. and Novak, A. *Infrared Spectra of and Hydrogen Bonding in Some Acid Salts of Carboxylic Acids*. University of Ljubljana (1960).

Received July 4, 1968.