

Diffraction of X-Rays by Aluminum Dilaurate and Aluminum Distearate

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SOME information about the crystal structure of sodium soaps can be obtained despite the lack of single crystals. In the sodium soaps of saturated fatty acids, fibers occur naturally and excellent fiber diagrams were obtained (1). In the oleates, which are unsaturated, fibrillation was induced by extrusion through an orifice under pressure (2).

The aluminum soaps do not produce fibers, even on slow crystallization, nor could a fiber diagram be obtained from threads extruded under pressure. Only powder diagrams have been obtained. Like powder diagrams of other soaps, however, they have been useful in giving unambiguous values of the long spacings, arising from planes generally indexed as $00l$. The values obtained are of a magnitude that would necessarily lead to the fatty acid chains being placed end to end in pairs in the unit cell.

One crystalline form each of aluminum dilaurate and aluminum distearate yield x-ray patterns so nearly alike that they may be assumed to have similar crystalline structures. In other publications to appear from this laboratory these are called the "B₂ types." They are produced by precipitation above 80°C., an aqueous solution of potassium stearate or laurate being added to an excess of aqueous aluminum chloride, with vigorous stirring, followed by extraction of the dried precipitate with boiling acetone. They have been definitely established to be pure di-soaps, $AlOH \cdot Str_2$ and $AlOH \cdot L_2$. The microphotometer tracings of those two diagrams are reproduced in Figures 1 and 2, with the value of the corresponding Bragg spacing, d/n , in Ångström units beside each peak. Two sets of peaks may be distinguished. Those closer to the center correspond to successive orders of the long spacing, $c \sin \beta$, and those grouped between 6Å and 3Å correspond to short spacings.

Some of the short spacings correspond in the two soaps hence are independent of the length of the hydrocarbon chain and give strong indication of similarity in the crystal structure.

The normal configuration of paraffin chain crystals in compounds of relatively short chain-length, such as laurate and stearate radicals, is full extension of the chain, except for the zig-zag necessitated by the tetrahedral angle of the carbon bonds. The chains are placed end to end, sodium to sodium, methyl group to methyl group. The fully extended chains, however, may either be perpendicular to the terminal planes, as in orthorhombic unit cells with $d_{001} = c$, or inclined to the terminal planes, as in monoclinic unit cells with $d_{001} = c \sin \beta$, where β is the monoclinic angle between the c and a axes. For aluminum distearate and aluminum dilaurate the values of d_{001} are both less than would be calculated for the double length of the chains, assuming full extension and usually accepted bond distances. This indicates an inclined c -axis and a crystal system probably monoclinic.

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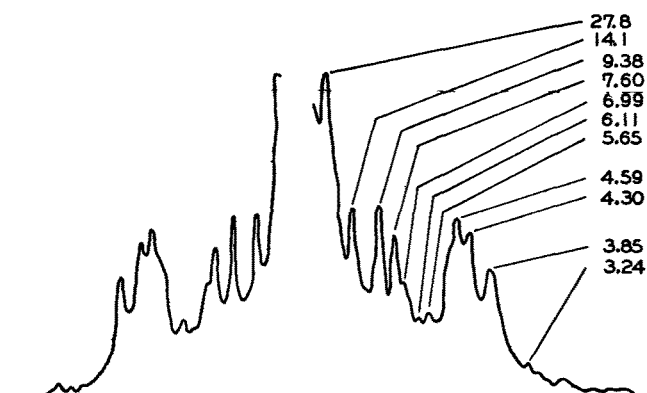


FIGURE 1 ALUMINUM DILAURATE

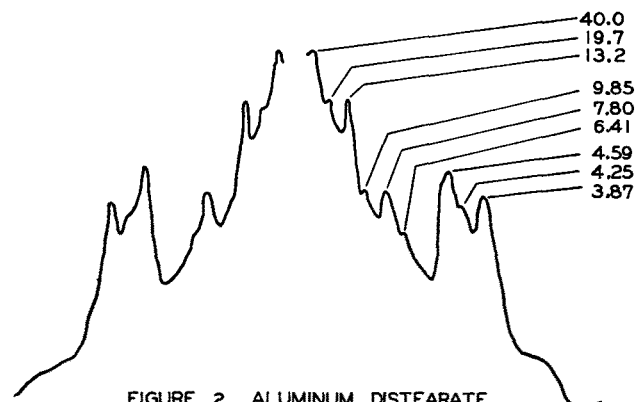


FIGURE 2 ALUMINUM DISTEARATE

Distance—Sample to plate—5 cm.
Magnification—2×.
Bragg spacings in Ångström units.

FIGS. 1 and 2. Microphotometer tracings of x-ray diffraction patterns. Aluminum dilaurate. Aluminum distearate.

All the lines in the x-ray patterns of the aluminum soaps corresponding to long spacings arise from successive orders of diffraction by the single long spacing of 28.1Å for aluminum dilaurate and 39.4Å for aluminum distearate. The difference 11.3Å = $\Delta c \sin \beta$. Since the distance between alternate carbon atoms in a hydrocarbon chain is 2.54Å, the corresponding value of Δc , for double molecules, is $6 \times 2.54 = 15.2\text{Å}$. The ratio of $\Delta c \sin \beta$ to Δc is $\sin \beta$ and equal to 0.741. Hence $\beta = 48^\circ$.

The double length of a sodium stearate molecule is known to be 52.2Å. If this were multiplied by $\sin 48^\circ$ the spacing for the two layers of sodium stearate molecules laid end to end would be 38.7Å whereas the observed spacing for the aluminum distearate is 39.4Å. Hence we must assume a double layer of aluminum atoms, corresponding to the double layer of sodium atoms. The general system of packing of molecules in soap crystals has been shown by McBain, Bolduan, and Ross (3).

Various possible arrangements of the hydrocarbon chains with respect to the aluminum atom are shown in Figure 3. In the first of these depicted the two

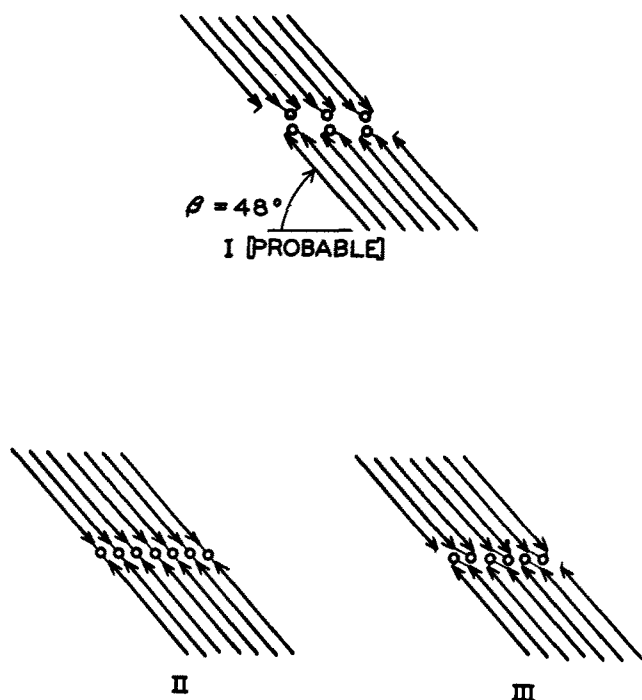


Fig. 3. Diagrams representing probable (I) and some excluded alternate arrangements (II-III) for the fatty acid chains of aluminum di-soaps.

chains connected with each aluminum atom are shown lying side by side. This is the only arrangement

among those shown which is in accord with the observed values for the long x-ray spacings. As in the sodium soaps, the aluminum atoms are arranged in a double row with the double hydrocarbon chains side by side and end to end.

Aluminum distearate produced by precipitation below 60°C ., followed by extraction with acetone at 30°C . or below, is referred to in this laboratory as "A₂ type." It is characterized by a long spacing of 47.4\AA and a single strong side spacing of 4.26\AA . Comparison with the long spacing described above would lead to a monoclinic angle of 60° for the "A₂ type" of aluminum distearate.

Summary

The aluminum di-soaps appear to have a crystal structure analogous to the sodium soaps, that is, the metal atoms are arranged in a double layer from which the fatty acid radicals extend in opposite directions, end to end. Hence in the aluminum di-soaps the two acid radicals attached to any aluminum atom lie side by side. Aluminum di-soaps produced by precipitation and extraction at higher temperatures have a monoclinic angle of 48° . Those produced at low temperature and extracted at low temperature have a higher value, β , of 60° .

REFERENCES

1. McBain, J. W., Bolduan, O. E. A., and Ross, S., *J. Am. Chem. Soc.*, **65**, 1873 (1943); Bolduan, O. E. A., McBain, J. W., and Ross, S., *J. Phys. Chem.*, **47**, 528 (1943).
2. Ross, S., and McBain, J. W., *J. Am. Chem. Soc.*, **68**, 296 (1946).
3. McBain, J. W., Bolduan, O. E. A., and Ross, S., *J. Am. Chem. Soc.*, **65**, 1876 (1943).

Report of the Spectroscopy Committee

THE Spectroscopy Committee has been but recently organized and as yet is not entirely complete as to personnel. The committee to-date is composed of the following members:

- B. W. Beadle—American Meat Institute, Chicago, Ill.
Ultraviolet spectra.
- B. F. Daubert—Univ. of Pittsburgh, Pittsburgh, Pa.
X-ray of fats.
- R. H. Ferguson—Procter and Gamble, Cincinnati, O.
X-ray of soaps.
- R. T. Milner—Northern Reg. Res. Lab., Peoria, Ill.
Visible spectra.
- R. T. O'Connor—Southern Reg. Res. Lab., New Orleans, La.
Emission spectra.
- R. C. Stillman—Procter and Gamble, Cincinnati, O.
Chairman.

A member familiar with infrared and Raman spectra is still to be appointed.

At the Fall meeting of the Society the Spectroscopy Committee was asked to cooperate with the Thiocyanogen Analysis subcommittee and the Saturated Acids subcommittee of the Fat Analysis Committee in an attempt to correlate results (on fat compositions) determined by the various methods. At the moment, this is the only program before the Spectroscopy Committee. It is expected that other problems will develop as the committee gets into operation.

The work program can be readily divided into several parts, all of which are concerned with the spectrochemical (ultraviolet) analysis of naturally occurring oils.

1. Set up a uniform nomenclature for work on ultraviolet absorption.

2. Investigate various factors in the methods used for spectrochemical analysis, including a study of solvents, gas blanketing during isomerization, temperature of isomerization, calibration of instruments, etc.

3. Arrive at a standard method of calculation of fat compositions.

4. Run careful analyses on

- a. Cottonseed oil
- b. Soybean oil
- c. Linseed oil
- d. Corn oil
- e. Lard
- f. Tallow.

Pure samples of all of these oils have been obtained and will be analyzed by approximately twelve collaborators who are active in this work. These same samples will be distributed to the Thiocyanogen and Solid Acids subcommittees for their work.

5. Attempt to correlate the results of the various committees to see wherein the methods differ.

6. Extend the work at a later date to include pure acids other than natural oils as well as hydrogenated oils and fats.

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