

X-Ray Diffraction by Aluminum Soaps¹

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THE chief value of the x-ray diffraction pattern of an aluminum soap is as a "fingerprint," which gives information both as to the relative particle size and crystallinity, as deduced from the sharpness and texture of the pattern, as well as to the identity with or difference from a known form (1), as deduced from the position of the lines of the pattern.

The present article deals with evidence obtained concerning: 1. the various distinct "crystalline forms" of aluminum dilaurate and distearate soaps, 2. the presence of free and sorbed fatty acids in unextracted aluminum soaps, and 3. the binding of water by extracted aluminum soaps.

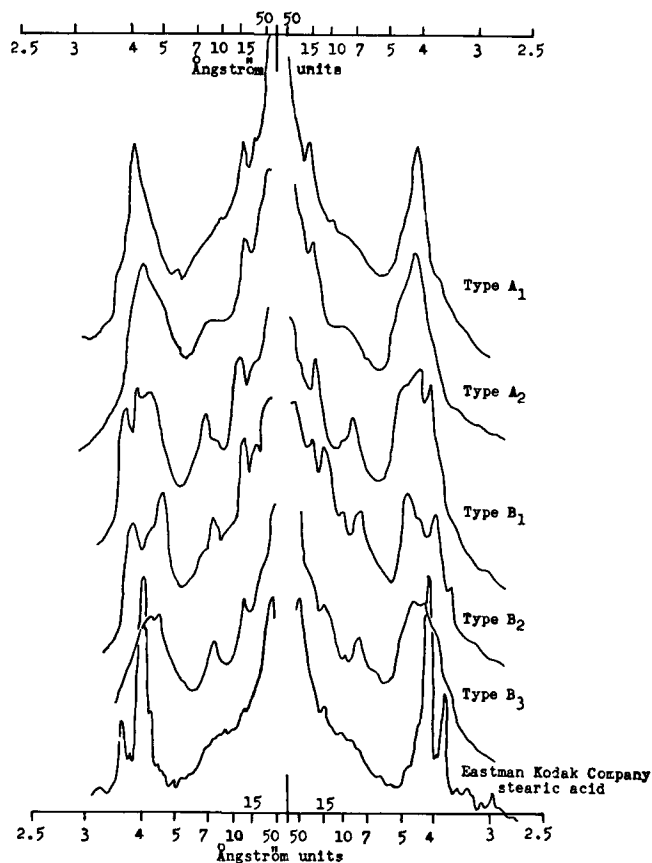


FIG. 1. Microphotometer tracings of x-ray diffraction patterns of five crystalline forms of aluminum distearate and of the reference stearic acid. Sample to film distance, 50 mm.

Only powder (Debye-Scherrer) diffraction patterns of aluminum soaps have been obtained because these soaps could not be produced as single crystals or even as well-formed fibers.

"Crystalline Forms" of Aluminum Distearate, $Al(OH)Str_2$

Fig. 1 shows microphotometer tracings characteristic of typical x-ray powder photographs obtained from different "crystalline forms" of aluminum distearate. Fifteen samples, prepared under a variety of conditions (2) and examined by x-ray diffraction, fell into one or another of the five pattern types shown in Table I. The specific "form" to which a sample belongs depends upon: a) the temperature at which it is precipitated, b) whether or not it is extracted, and c) the temperature at which it is extracted.

The patterns of the five "crystalline forms" differ in the position of their lines and halos, which is indicative of a change either of composition or of crystal type. As some of the samples are unextracted, stearic acid is present. Some of the Bragg spacings reported (see Table I) can be ascribed definitely to free stearic acid and they are indicated by being enclosed in brackets. When these spacings are left out of consideration, however, the original five forms still remain. Although they may not all be disparate "crystal forms" in the strict sense of the term, it is convenient to retain the classification of samples in five groups because of the frequency of their occurrence.

TABLE I

The Most Prominent Bragg Spacings of X-Ray Diffraction Patterns of Five Crystalline Forms of Aluminum Distearate and of the Eastman Kodak Company Stearic Acid from Which They Were Prepared

Type	Conditions of Preparation	Long Spacing* (Å)	Short Spacings	
			Intensity**	d/n (Å)
A ₁	Cold precipitation (60°C. or below), unextracted	49.5 ± 0.5	m	4.60 ± 0.05
			s	(4.12 ± 0.03)
A ₂	Cold precipitation (60°C. or below), cold extraction (30°C. or below)	47.4 ± 0.8	w	7.8 ± 0.1
			vw	4.7 ± 0.1
			vs	4.26 ± 0.1
B ₁	Hot precipitation (80°C. or above), unextracted	42.0 ± 0.5	s	7.7 ± 0.1
			s	4.60 ± 0.03
			vs	(4.11 ± 0.03)
			s	3.85 ± 0.03
B ₂	Hot precipitation (80°C. or above), hot or cold extraction	40.0 ± 0.5	w	7.8 ± 0.1
			m	7.44 ± 0.05
			s	4.65 ± 0.03
			m	4.20 ± 0.03
			s	3.85 ± 0.03
B ₃	Cold precipitation (60°C. or below), hot extraction (boiling acetone)	42.0 ± 0.5	m	7.8 ± 0.1
			s	4.68 ± 0.05
			s	4.26 ± 0.03
			w	3.85 ± 0.03
....	Eastman Kodak Company Stearic Acid	40.0 ± 0.5	s	4.57 ± 0.05
			vs	4.13 ± 0.03
			w	3.85 ± 0.03
			m	3.65 ± 0.05
			m	2.46 ± 0.03

* These were averaged from the first, second and third orders of the long spacing, which are mostly strong, weak, and medium, respectively.

** s = strong, m = medium, w = weak, v = very.

When an unextracted aluminum stearate is freed (2, 3,) from uncombined acid to give di-soap, considerable change may occur in the crystal structure, as when the A₁ form of aluminum distearate is changed to the B₃ form, with an accompanying 20% difference in long spacing. On the other hand, the

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change may be much smaller, as when the A_1 form changes to the A_2 , or the B_1 to the B_2 upon extraction of all uncombined acid. The latter changes are associated with changes in spacing so small that both forms may have similar crystalline structures, slightly distorted in the unextracted samples by the presence of sorbed fatty acid.

In the case of pure sodium soaps there have been established for any one soap a large number of x-ray powder patterns (4). Many of these are similar to each other. They come from closely related but definitely different monoclinic forms. Judging from the neutral sodium soaps and the corresponding acid sodium soaps, the small change in x-ray pattern between A_1 and A_2 or B_1 and B_2 would appear not to be due to the acid being held in the form of a new compound because its structure would be expected to be very different. Neither is the acid sorbed by exterior surfaces alone, which would have left the crystal structure unchanged. The presence of the sorbed acid distorts or slightly rearranges the crystal structure but the mechanism involved has not been elucidated.

The two forms of aluminum dilaurate which are analogous to the B_1 and B_2 forms of aluminum distearate are shown in Figure 2. The characteristic Bragg spacings of the former are reported in Table II.

TABLE II

The Most Prominent Bragg Spacings of X-Ray-Diffraction Patterns of Unextracted and Extracted Aluminum Dilaurate and of the Eastman Kodak Company Lauric Acid from Which They Were Prepared

Conditions of Preparation	Long Spacing* (Å)	Short Spacing	
		Intensity**	d/n (Å)
Unextracted $Al(OH)L_2$	30.0 ± 0.5	m	7.8 ± 0.1
		m	4.58 ± 0.05
		s	(4.13 ± 0.05)
		m	(3.75 ± 0.05)
Extracted $Al(OH)L_2$	28.1 ± 0.5	m	7.7 ± 0.1
		m	4.59 ± 0.05
		m	4.30 ± 0.05
		m	3.85 ± 0.05
Eastman Kodak Company Lauric Acid	27.4 ± 0.5	m	4.85 ± 0.05
		s	4.58 ± 0.05
		s	4.37 ± 0.05
		vs	4.13 ± 0.05
		s	3.76 ± 0.05

* These were averaged from the first, second, and third orders of long spacing.

** s = strong, m = medium, w = weak, v = very.

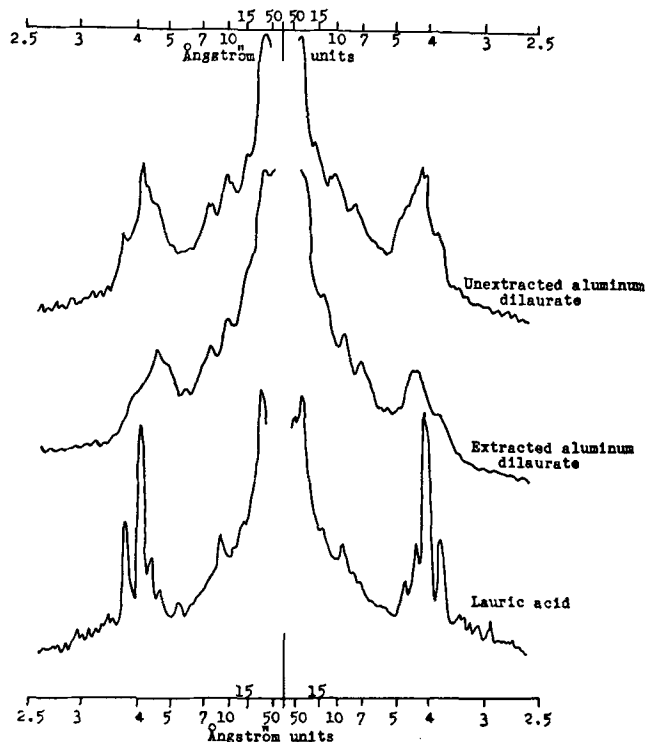


FIG. 2. Microphotometer tracings of x-ray diffraction patterns of extracted and unextracted crystalline forms of aluminum dilaurate and of the reference lauric acid. Sample to film distance, 50 mm.

"Crystalline Forms" of Aluminum Dilaurate, $Al(OH)L_2$

An examination of x-ray powder diffraction patterns of 10 different samples of aluminum dilaurate has indicated that they all consist of one of two crystalline forms (1). In contrast to the distearate, the form obtained depends only on whether the dilaurate is extracted or unextracted; neither the temperature of preparation (25-100°C.) nor the temperature of extraction affects the form obtained. No other polymorphs were produced by varying these two conditions.

Evidence for the Presence of Free Acid in Aluminum Di-Soaps

It has been commonly taken for granted that metathetic preparation leads to aluminum tri-soaps—those of commerce—if the reagents are merely taken in those proportions. However, McBain and McClatchie (5) have shown that no matter how carefully prepared, some fatty acid is immediately extracted with the dry solvent, showing that some acid is not chemically combined. More recent extraction experiments indicate that 20-30% of free or loosely bound fatty acid is unavoidably precipitated along with the aluminum di-soap. It was of interest to know whether this fatty acid was molecularly sorbed, free (i.e., as crystals with activity substantially equal to that of pure-free acid), in solid solution, or finally perhaps combined with the soap in some manner such as in the formation of an acid soap. The following portion of this investigation, along with extraction experiments reported elsewhere (6), was carried out to elucidate this matter.

All of the extracted aluminum soaps we have obtained have particle size small enough that an x-ray powder diffraction picture shows smooth continuous lines. However, it was noticed that one sample of unextracted aluminum stearate, precipitated at 0°, showed a definite graininess or unevenness of some of the lines. A closer examination revealed that the grainy and uneven lines corresponded to the stronger lines of stearic acid alone while the smooth lines were close to those found for the extracted di-soaps and not found for the acid. This fortunate circumstance allowed the ascription of some of the lines in the x-ray diagram of the unextracted stearate to the free fatty acid, and others to the di-soap containing lightly bound acid. By analogy, the same could be done for the x-ray diagrams of the dilaurates. Prepared mixtures of extracted di-soap and finely powdered acid confirmed the correctness of the interpretation. The stearic acid was a mixture of the "B" and "C" forms of Francis, Piper, and Malkin (7), prepared by crystallization from acetone solution.

Most of the lines of the acid are either super-imposed upon or so close to lines from the soap that they cannot be used for qualitative identification unless the acid is present in large quantities. However, there are lines from two short spacings which identify the fatty acid:

a) A very intense line at 4.13 Å which is present in both stearic and lauric acids. This line almost coincides with the lines of the di-soaps in the region of 4.2 Å, but its great intensity and its unevenness or "spottiness" make it distinguishable from these lines.

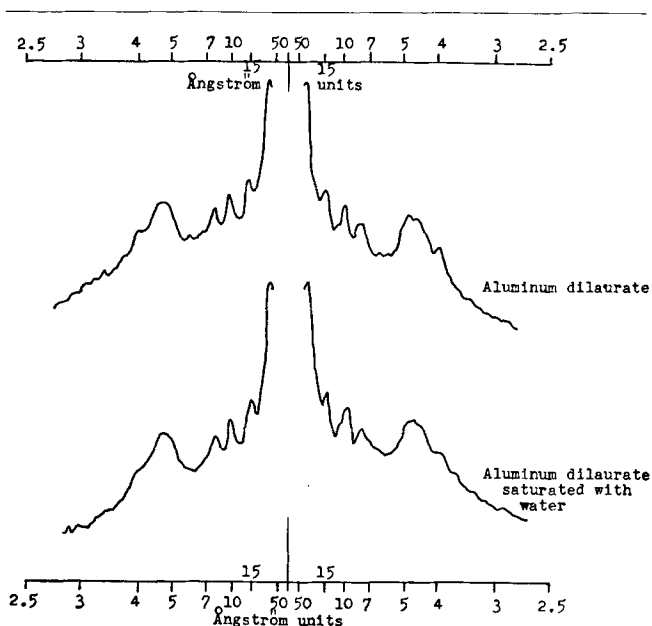


FIG. 3. Microphotometer tracings of aluminum dilaurate, dry, and saturated with water. Sample to film distance, 50 mm.

b) A line at 3.67 Å for the stearic acid and 3.75 Å for the lauric acid. These are far enough from any lines of the aluminum di-soaps to be easily visible, but they are not as intense as the 4.13 Å line.

The potassium soaps from which the aluminum soaps were prepared did not have any spacings that might be mistaken for the above mentioned spacings of the acid.

An examination of our x-ray diffraction patterns shows that all those for the unextracted soaps, containing about three-quarters of an equivalent of acid in excess of that required for the di-soap, show the characteristic fatty acid lines, which are absent from the patterns of the extracted soaps. From a comparison of the intensity of the lines in the soaps and in prepared mixtures containing known amounts of acid, it is estimated that the amount of free acid present is of the order of 5 to 10%, in the case of the unextracted distearate. This is the same order of magnitude as found by thorough extraction. In the

case of the aluminum dilaurate, the amount of free acid appears to be much larger, of the order of 25%.

The Binding of Moisture by Aluminum Soaps

Aluminum di-soaps after heating in high vacuum (McBain-Baker method) are somewhat hygroscopic (8) and can fix an amount of water interpretable as involving formation of a hemi-hydrate. This moisture, however, does not produce any significant change in x-ray diffraction pattern, as shown in the tracings of Figure 3. They were obtained from diffraction patterns produced by the same portion of soap enclosed in a sealed, thin-walled capillary in a fixed position on the x-ray collimator. The aqueous tension to which the soap was exposed was varied from saturation to 10.0006 mm. Hg by a method already described (9). The absence of change in crystal structure shows that water is held by surface forces only.

Summary

1. The microphotometer tracings and Bragg spacings of typical x-ray powder diffraction patterns are reported for aluminum dilaurates and distearates. Patterns for both extracted soaps and soaps containing uncombined acid are included. The extraction of molecular, uncombined fatty acid may produce either a complete recrystallization of the soap, or only minor changes in the diffraction pattern. At least two of the three types of extracted distearate are polymorphs whereas the two types of unextracted stearate are each mixtures of free fatty acid, together with what may be a solid solution of fatty acid in one of the extracted types.

2. Extracted aluminum dilaurate has been observed to exist in only one "crystalline form," differing from that of the unextracted aluminum dilaurate. The latter consists of free fatty acid, together with dilaurate sorbing some acid with a slight but distinct change in the x-ray powder pattern.

3. The presence of some free fatty acid in unextracted aluminum soaps is confirmed by x-rays.

4. The sorption of moisture has no effect on the x-ray diffraction pattern of aluminum di-soaps, pointing to purely surface attachment of water.

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