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X-Ray Diffraction Studies of the Metal Soaps of Fatty Acids of Odd Carbon Numbers

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Synopsis. X-Ray diffraction patterns have been observed for metal soaps of fatty acids with odd carbon numbers. The soaps of Pb, Cd, Ba, and Zn were prepared from the fatty acids of hexanoic, heptanoic, nonanoic, decanoic, undecanoic, dodecanoic, tridecanoic, tetradecanoic, pentadecanoic, hexadecanoic, heptadecanoic, and octadecanoic, the long spacings of which were studied in comparison with those of sodium soaps. The most prominent characteristic of these soaps is the presence of a definite order of long spacing which is directly proportional to the number of carbon atoms in the hydrocarbon chains, this is in contrast to the sodium soaps, which show a zigzag relation.

Although many reports have been presented on X-Ray diffraction studies on metal soaps, they have been concerned with the fatty acid salts of even carbon numbers originating from natural fatty oils.[1-6)]

Recently, though the advance of organic synthesis has made the fatty acids of odd carbon numbers readily available for technical uses. It is important to investigate the properties of metal soaps of fatty acids with odd carbon numbers to facilitate the present industrial activity. With this in view, X-Ray diffraction patterns have been obtained for the metal soaps of fatty acids of odd carbon numbers in this study.

Experimental

Materials. *Fatty Acids*: The fatty acids, from hexanoic acid (C_6) to octadecanoic acid (C_{18}), used in this investigation were supplied from the Ajinomoto Co., Ltd. The purities of the fatty acids were confirmed to be over 98.5 per cent by gas chromatography.

Metal Salts: The inorganic chemicals used in the preparation of metal soaps were a reagent grade: lead acetate $Pb(CH_3COO)_2$, cadmium sulfate $CdSO_4$, barium nitrate $Ba(NO_3)_2$, and zinc acetate $Zn(CH_3COO)_2$.

Preparation of Metal Soaps. The soaps of Pb, Cd, Ba, and Zn were prepared by the addition of aqueous solutions of sodium soaps to a large excess of solutions of the metal salts. The precipitates were washed with water and then with ethanol, and successively extracted with boiling acetone. The purified metal soaps were dried *in vacuo* and then stored in a desiccator at room temperature for two months.

Apparatus. The X-ray diffraction measurements were performed with a Rigaku Denki Geiger Spectrometer D-9C instrument, using copper K_α radiation through a nickel filter, under the following conditions: voltage, 30 kV; 10 mA; count full scale, 1000 c/s; scanning speed, 2/min; time constant, 2 cm/min.

Results and Discussion

X-Ray diffraction patterns were obtained for a series of metal soaps made from straight-chain fatty acids containing 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, and 18 carbon atoms. Figure 1 shows the X-Ray diffraction patterns of the metal soaps of tridecanoic acid in comparison with the sodium soap.

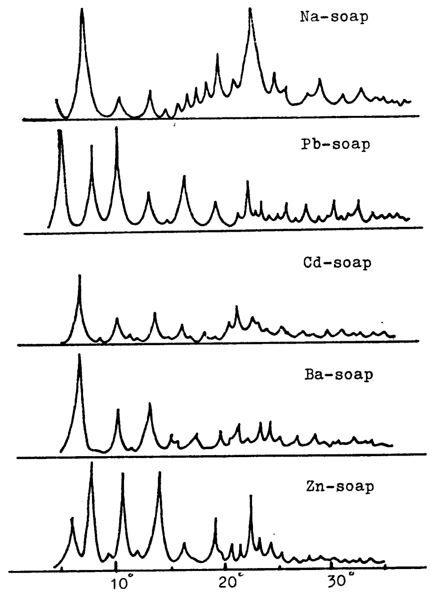

Fig. 1. X-Ray diffraction pattern of metal soaps of tridecanoic acid.

All of the metal soaps showed several strong diffraction patterns corresponding to the spacings. It is noticed that sodium soap diffracts strongly, showing the higher crystallinity of sodium soaps than those of the other metal soaps. Similar results were also obtained for the metal soaps of the other fatty acids.

In Table 1, the long spacings for the metal soaps of

TABLE 1. LONG SPACING (Å) OF METAL SOAPS

Carbon number of fatty acid	Na-soap	Pb-soap	Cd-soap	Ba-soap	Zn-soap
C_{18}	48.21	51.27	50.01	48.10	42.70
C_{17}	45.17	48.87	47.90	46.35	41.88
C_{16}	42.75	46.50	45.72	44.17	38.46
C_{15}	39.00	43.47	42.46	40.56	36.05
C_{14}	37.35	41.43	40.17	38.43	34.02
C_{13}	33.99	37.89	36.84	35.85	33.12
C_{12}	32.34	35.37	34.47	32.72	—
C_{11}	29.16	33.00	32.37	30.48	27.98
C_{10}	27.83	30.84	30.15	28.53	26.01
C_9	24.57	28.23	26.01	25.77	23.49
C_8	23.28	25.77	22.68	—	20.91
C_7	20.28	23.28	20.91	—	—
C_6	20.13	20.70	20.58	—	—

Table 2. Short spacing of metal soaps

	Short spacing (Å)				
	(i) C_{16}-soaps				
Na-soa&	4.60(m)	4.17(m)	3.87(ss)	3.56(m)	—
Pb-soap	4.10(ss)	3.93(m)	3.82(m)	3.66(s)	—
Cd-soap	4.08(ss)	3.90(m)	3.19(s)	3.68(m)	—
Ba-soap	4.57(s)	4.04(m)	3.90(s)	3.72(s)	—
Zn-soap	4.55(s)	4.33(m)	4.04(m)	3.85(ss)	—
	(ii) C_{13}-soaps				
Na-soap	4.91(s)	4.19(m)	3.87(ss)	3.56(m)	—
Pb-soap	4.21(m)	4.08(ss)	3.85(m)	3.79(w)	3.65(m)
Cd-soap	4.12(m)	3.78(m)	3.53(w)	—	—
Ba-soap	4.60(m)	4.42(m)	4.35(m)	4.01(m)	3.80(m)
Zn-soap	4.62(ss)	4.27(m)	4.15(m)	4.10(ss)	3.80(m)

fatty acids with even and odd carbon numbers from C_6 to C_{18} are shown. The short spacings for metal soaps of hexadecanoic and tridecanoic acid are shown in Table 2. The short spacings permit the identification of the soaps.

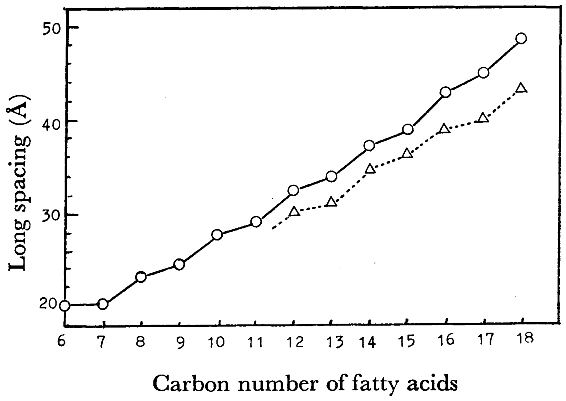

Fig. 2. Long spacing of sodium soaps in reference with those of fatty acids.
○; Sodium soap, △; fatty acid.

Figure 2 shows the long spacings of the sodium soaps and the fatty acids. The data for the fatty acids are taken from the literature.[7,8] Here, the crystalline forms of the acids are denoted as the B-form for even-carbon-number acids and as the B′-form for odd-carbon-number acids.

When the long spacings of the sodium soaps of saturated fatty acids are plotted against the number of carbon atoms, as in Fig. 2, one obtains a zigzag curve (high at even carbon numbers and low at odd). It is also well known that the long spacings of fatty acids are related to the carbon numbers of the fatty acids in a zigzag curve.

On the other hand, the melting points of saturated fatty acids with even and odd numbers of carbon atoms are known to be related to the carbon number in a zigzag curve with higher melting points for the even fatty acids than those for the odd ones. This is because fatty acids with odd carbon numbers have structures of the *cis*-form, by analogy with other organic compounds showing long and short terminal distances between two adjacent molecules when the molecules are declined, while the fatty acids with even carbon numbers have structures of the *trans*-form showing a short terminal distance only. Therefore, the packings of fatty acids with odd carbon numbers are more loose than those of even ones.

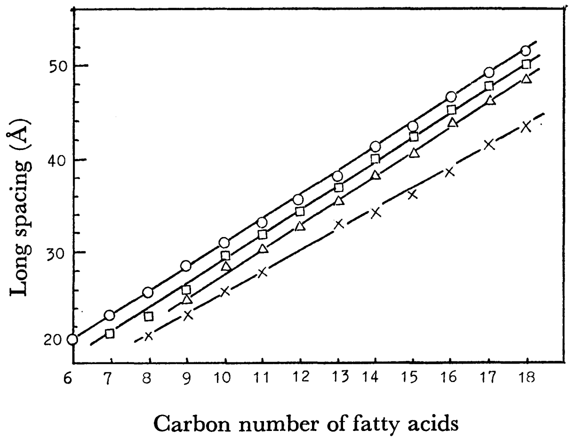

Fig. 3. Long spacing of metal soaps.
○; Pb-soap, □; Cd-soap,
△; Ba-soap, ×; Zn-soap.

Figure 3 shows plots of the long spacings of the metal soaps against the carbon numbers of the fatty acids. It may be noted in the figure that the long spacings of these metal soaps increase linearly with the number of carbon atoms in the fatty acids.

Vold *et al.*[4] have reported that the long spacings of heavy metal soaps are correlated with their structures, in which the cations are separated in parallel planes at a distance somewhat less than the length of two fatty acid radicals. In this work, it was found that the regular increase in spacing (about 2.5 Å per additional carbon atom) corresponds to twice the size of the CH_2 unit.

However, the slope of the linear relation for Zn-soap differs from those of the other metal soaps. Matuura[6] found that the long spacings for the soaps of fatty acids with most of the light metals in the periodic table appear to be peculiar. The peculiarity of Zn-soaps seems to be related to Matuura's result. The theoretical approaches to the details of this evidence will be here after studied.

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