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Studies of Helical Aggregates of Molecules. II. The Sense of Twist in the Fibrous Aggregates from the Alkali Metal Soaps of Optically Active 12-Hydroxystearic Acid

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Under an electron microscope, it was observed that the alkali metal soaps of 12-D(or L)-hydroxystearic acid separated out twisted fibers from various solutions. A symmetrical relationship regarding the sense of the twist was found between the soap fibers of the D-enantiomer and those of the L-enantiomer. In the case of the soap fibers of the D-enantiomer, the sense of twist was right-handed for the Li soap and left-handed for the Rb and Cs soaps. The Na- and the K- soap fibers produced both right-handed and left-handed fibers. A solvent effect with respect to the sense of twist was found for the fibers of the free acid and its Li soap. The cause of the twisting was discussed in connection with the structure and the growth process of the soap crystal.

In the preceding paper[1] we reported that optically active 12-hydroxystearic acid and its lithium soap produced twisted fibers when allowed to crystallize out from appropriate solvent and that the sense of twist is related to the optical isomerism of this hydroxy acid. Studies have since been extended to other univalent metal soaps, as has been described in part in a preliminary report.[2]

1) T. Tachibana and H. Kambara, This Bulletin, **42**, 3422 (1969).

2) T. Tachibana and H. Kambara, *J. Colloid Interfac. Sci.*, **28**, 173 (1968).

The sense of twist has been found to be associated with the cation size. This paper will describe the results obtained mainly with a series of the alkali metal soaps; the solvent effect on the sense of twist is also included.

Experimental

The purification of D-12-hydroxystearic acid from the commercial product and the preparation of L-12-hydroxystearic acid have been described previously.[1] The alkali metal soaps were prepared by neutralizing the acid with the desired metal hydroxide in anhydrous ethanol or in aqueous ethanol, by then recrystallizing several times from ethanol, and finally by drying over P_2O_5 *in vacuo*. The purity of these soaps was checked by elementary analysis, infrared absorption spectroscopy, and differential thermal analysis. The infrared spectra of these samples showed no peak at about 1700 cm^{-1} (the C=O stretching vibration for carboxylic acid) or at from 1600 to 1650 cm^{-1} (the deformation vibration for water). The absence of water was also confirmed by the use of differential thermographs. These results show that these soaps were reasonably pure and in an anhydrous form. The sample of the Rb soap was mixed with the K soap, since it was prepared by using RbOH, which had been found by fluorescent X-ray analysis to contain K in a Rb/K ratio of 80/20.

The sample of the NH_4 soap was a gift of Dr. Yoshiro Tsutsui, who prepared it by reacting the D-acid with liquid ammonia under 59 atm at 110°C for 24 hr in an autoclave.

The Ag soap was prepared by the metathesis of the Na soap in aqueous ethanol in a dark room.

The Tl(I) soap was prepared by neutralizing the D-acid in ethanol with an aqueous solution of thallous hydroxide.

The soap fibers are formed in the grease or the gel, which is made by dissolving the soap in a solvent at a high temperature and by then cooling the hot solution to room temperature. Since it was considered that the free acid may have been formed by the thermal decomposition of the soap during the preparation of the grease, the soap samples recovered from the grease were subjected to infrared analysis. It was confirmed that these samples contain no free acid.

The procedure of observing the fibers by means of an electron microscope was described in the preceding paper.[1]

Results

a) The Alkali Metal Soaps. Under the electron microscope, the grease or gel from the soaps was observed to consist of twisted fibers with a certain thickness, the thickness being dependent on the procedure used in making the grease. Figure 1 shows typical micrographs of the fibers of the alkali metal soaps.

As has been stated previously,[1] the Li soap produced twisted fibrils about 0.03 μ in width from ethanol, while helical ribbons of from 0.03 to 0.3 μ in width were produced from mineral oil and from Nujol. The Na and K soaps formed twisted fibers and ribbons from 0.02 to 0.3 μ in width, depending on the conditions used in the grease preparation. The Rb and Cs soaps produced ribbons of the form characteristic of these soaps, in addition to the fibers of a form such as was observed in the other alkali metal soaps.

The sense of twist was characteristic of the respective soaps. It is represented, together with the results for the free acid, in Table 1; it is found that

Table 1. The sense of twist in the fibers from both enantiomers of 12-hydroxystearic acid and their alkali metal soaps

Enantiomer	The sense* of twist					
		Alkali metal soap				
	Acid	Li	Na	K	Rb	Cs
D	l	r	r&l	r&l	l	l
L	r	l	r&l	r&l	r	r

* r: right-handed twist, l: left-handed twist

there is an enantiomorphic relationship between the D-enantiomer and the L-enantiomer for the alkali metal soaps as well as for the free acid. From this table, it can be seen also that the sense of twist for the soaps of the D-acid changes from right to left with an increase in the cation radius; it is right-handed for the Li soap of the D-acid, while it is left-handed for the Rb and Cs soaps of the D-acid.

The Na and K soaps, which occupy the intermediate positions, did not always give reproducible results. Usually, but not always, they were inclined to exhibit both right-handed fibers and left-handed fibers from the same sample. In detail, the same sample of the Na soap or the K soap produced either of these fibers alone on one occasion, and both right-handed and left-handed fibers at the same time on another occasion. In the latter case, the right-handed and the left-handed fibers appeared as separated groups, either group being predominant. These results led us to draw a hasty conclusion in a previous communication[3] that the sense of twist was always right-handed for the Na and K soaps.

Since the non-reproducible results were considered to be due to the slight difference in the soap samples, a further investigation was made with the samples of the Na and K soaps, which had been prepared by the reaction of the D-acid in its ethanol solution, (1) with an NaOH (or KOH) aqueous solution, (2) with an NaOH (or KOH) ethanol solution, and (3) with Na (or K)-alcoholate. The samples thus obtained showed identical infrared absorption spectra, X-ray diffraction patterns, and differential thermographs, indicating that they

3) T. Tachibana and H. Kambara, *J. Amer. Chem. Soc.*, **87**, 3015 (1965).

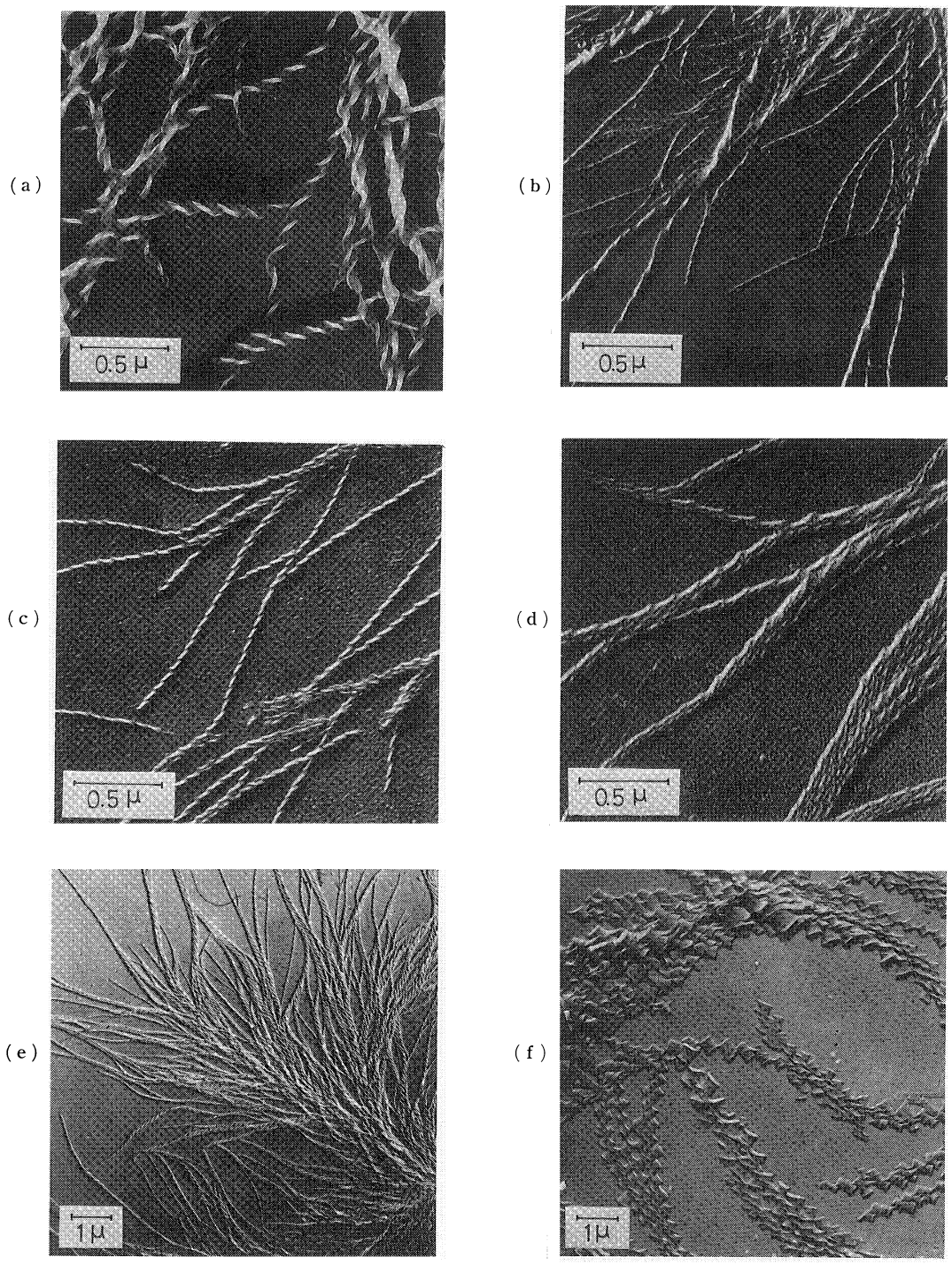
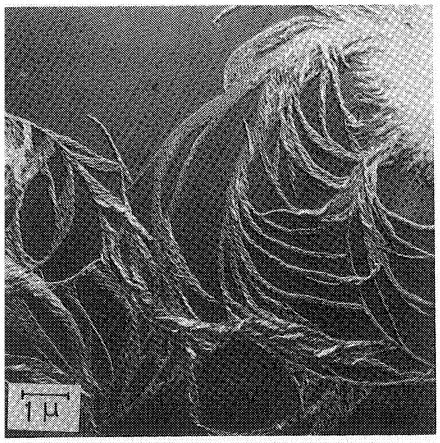
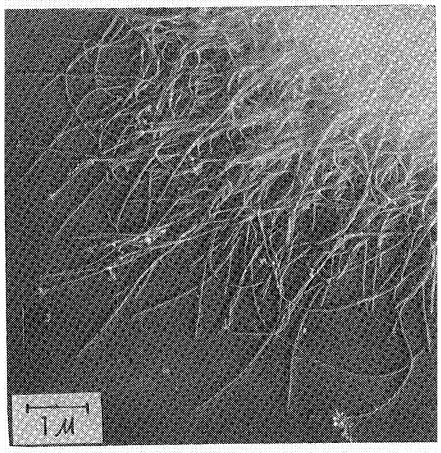


Fig. 1. The twisted fibers of the alkali metal soaps of D-12-hydroxystearic acid.
(a) Li soap from mineral oil, right-handed twist.
(b) Na soap from ethanol, right-handed & left-handed twists.
(c) K soap from hexanol, right-handed twist.
(d) K soap from nonanol, left-handed twist.
(e) Rb soap from hexanol, left-handed twist.
(f) Cs soap from hexanol, left-handed twist.

(a)



(b)



(c)

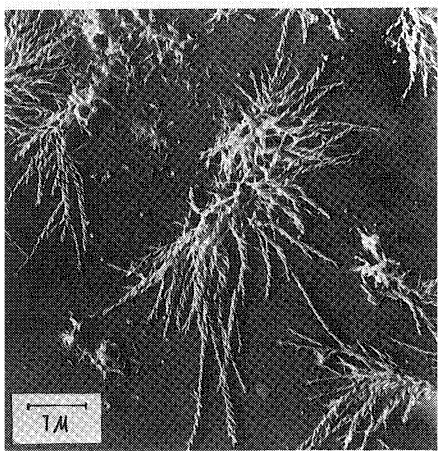


Fig. 2. The twisted fibers of the NH_4, Ag and Tl soaps of D-12-hydroxystearic acid.
(a) NH_4 soap from ethanol, left-handed twist.
(b) Ag soap from ethanol, left-handed twist.
(c) Tl soap from *n*-butanol, left-handed twist.

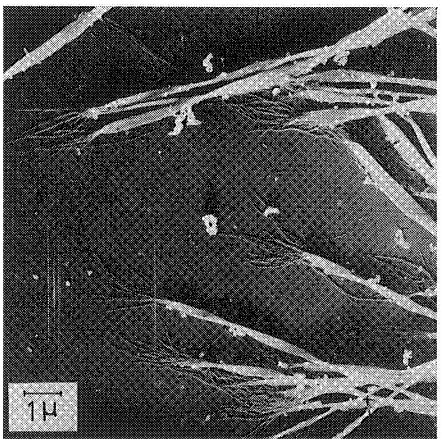


Fig. 3. The twisted fibers of D-12-hydroxystearic acid from nonanol.

belong to the same crystalline phase. Moreover, it was confirmed from these measurements that these samples are samples of the neutral soap, but not so-called acid soaps. The greases were prepared from these samples under the same conditions as far as was possible; consequently, all of the greases gave the same results. These Na-(or K-) soap samples produced both right-handed fibers and left-handed fibers from mineral oil or Nujol as well as from ethanol. Each fiber appeared as a separated group from the same sample; for the Na-soap fibers from mineral oil or Nujol, one group consisted of uniformely-thin fibrils with a right-handed twist, and another, of wide ribbons with a left-handed or right-handed twist. One may consider the possibility that the left-handed fibers consist of the free D-acid produced by the thermal decomposition of the Na soap during the preparation of the grease. However, the infrared analysis showed no free acid in the sample of the Na soap recovered from the grease. Therefore, the fact that both fibers were produced from these samples of the Na soap is to be ascribed to a property of this metal soap. Almost the same result was also obtained in the case of the K soap. Probably, the fibers twist in either the right-hand or the left-hand direction as a result of some slight difference in the conditions under which the fibers are formed. It can thus be suggested that the energy difference which determines whether the Na(or K)-soap fibers twist to the right or to the left is very slight, so that the effect of the asymmetric molecule is obscured. On the other hand, the Li-soap fibers twist stably to the right, and the Rb- and the Cs-soap fibers do so to the left. On the basis of these results, a specific effect of the alkali-metal cations can clearly be seen on the sense of twist.

b) The Other Soaps. The NH_4, Ag, and Tl(I) soaps of the D-acid were also investigated. Figure 2 shows typical micrographs of the fibers of these soaps. Since the NH_4 soap is readily decomposed with a rise in the temperature, the crystallization was done in a refrigerator after the saturated solution in ethanol had been prepared at room temperature. The precipitate thus obtained was found to contain more or less the free D-acid by infrared analysis; it was found to consist of fibers of the left-handed twist alone. These results strongly suggest that the NH_4-soap fibers exhibit a left-handed twist.

The Ag soap produced left-handed fibers from its ethanol solution.

The Tl(I) soap produced left-handed fibers from its ethanol, *n*-butanol, or *n*-octanol solution, although sometimes right-handed fibers were included. From these results, it can be roughly concluded that the fibers from the univalent metal soaps of the D-acid having a cation of a comparatively large size are inclined to twist to the left.

c) The Solvent Effect. An investigation was made into the effect of various solvents on the sense of twist in the fibers from the free D-acid and from its soaps. When the solvents used for the preparation of the grease were mineral oil, Nujol, ethanol, carbon bisulfide, nitrobenzene, and dimethyl formamide, it was found that these solvents greatly affect the form of the twisted fibers produced, but they had no influence on the sense of twist.

When a series of *n*-aliphatic alcohols were used as the solvents, a notable effect on the sense of twist was found only for the free D-acid and its Li soap, the cation sizes of which are comparatively small. The results are shown in Table 2. The free D-acid and its Li soap produced both left-handed fibers and right-handed fibers from the solution in an alcohol of from C_6 to C_{10}, while from the shorter-chain (C_2 to C_4) alcohols the D-acid fibers exhibited only a left-handed twist, and the Li-soap fibers, a right-handed twist alone. No solvent effect on the sense of twist was found for the fibers from the Na, K, Rb, and Cs soaps.

TABLE 2. THE EFFECT OF *n*-ALIPHATIC ALCOHOLS AS THE SOLVENT ON THE SENSE OF TWIST IN THE FIBERS OF D-12-HYDROXYSTEARIC ACID AND ITS ALKALI METAL SOAPS

Sample	Carbon number of *n*-aliphatic alcohols as the solvent								
	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Free acid	l	l	l	r&l	r&l	r&l	r&l	r&l	r&l
Li soap	r	r	r	r	r&l	r&l	r&l	r&l	r&l
Na soap	r&l	r&l	r&l	r&l	r&l	r&l	r&l	r&l	r&l
K soap	r&l	r&l	r&l	r&l	r&l	r&l	r&l	r&l	r&l
Rb soap	l	l	l	l	l	l	l	l	l
Cs soap	l	l	l	l	l	l	l	l	l

r: right-handed twist, l: left-handed twist

The crystalline aggregates of the D-acid or its Li soap recovered from *n*-heptanol solution showed a melting point, an X-ray diffraction pattern, and an infrared spectrum identical to those of the samples from ethanol solution. This indicates that the observed effect is not due to the difference in the crystalline phase of the fibers produced. Probably, in any stage of the growth of the fibrous crystal the solvent molecules may act so as to obscure the asymmetrical effect of the enantiomer molecule through the solvation. Here it is interesting to note that the molecules of these alcohols approximate a fragment of 12-hydroxystearic acid molecules.

In this connection, it may be mentioned that cyclohexanol, which is a cyclic alcohol, did not exhibit this abnormal behavior, but functioned much like the normal C_2- to C_4-alcohols.

An attempt was made to investigate the effect of an optically-active solvent. The D-acid, the L-acid, and the respective soaps produced twisted fibers from solutions in optically active amyl alcohol (L-form). The results regarding the sense of twist

were quite identical with those with the solution in *n*-amyl alcohol. Accordingly, no effect of the optically-active solvent was observed.

Discussion

Twisted crystal shapes are not unique to soap fibers, but they have been observed for quartz and various whiskers. Wilman[4] explained such structures as the results of the rotational slip of crystal layers parallel to the cleavage plane. McClellan[5] explained the shape of soap fibers in terms of an equation derived by Eshelby,[6] who showed that a whisker containing an axial-screw dislocation must be uniformly twisted by an amount equal to the Burger vector of the dislocation divided by the crosssectional area of the whisker. However, the explanation that the twisting is a result of the dislocation seems doubtful in the case of the soap fibers, because it is difficult to explain why the Li soap of 12-D(or L)-hydroxystearic acid forms twisted fibers, whereas the racemic soap always forms non-twisted fibers.

All our findings described in the preceding paper and in the present paper have demonstrated that the sense of twist is determined by the chemical species and is, furthermore, dependent on the conformation of the molecule. Thus, the twisting should be explained by a mechanism which reflects the conformation of the molecule. Recently, in our laboratory, it has been found that the Na soap of a paraffin-chain fatty acid, for example, Na myristate, sometimes forms twisted fibers. In such a case, both right-handed and left-handed fibers are observed. Therefore, twisting is considered to be common for soap fibers and particularly likely in fibers with such asymmetric molecules as optically active 12-hydroxystearate.

Generally the crystal of a paraffin-chain compound is composed of alternating ionic and hydrocarbon layers. While the complete crystal structure determination has not yet been achieved for 12-hydroxystearic acid and its soaps, they may be regarded as being composed of such a layer structure, since these compounds also showed a long spacing, about 48 Å, in the X-ray powder patterns. Bird and Rooney[7] presented evidence of such a structure for Ca-soap fibers from a commercial fatty acid; they obtained that evidence by means of a high-resolution electron microscope. This structure must be responsible for the growth of the soap crystal in the form of a ribbon or a fiber.

If one of the surfaces of a thin ribbon is different from another surface in the structure, the distortion or twisting will tend to occur as a result of a surface stress which develops from the difference in the surface energy between the two surfaces. When the soap ribbon is produced from such a nonpolar solvent as Nujol, free-energy considerations require the development of the nonpolar surfaces in a manner that exposes the methyl groups to Nujol. Consequently, both surfaces of the ribbon would have the same structure, and would thus not cause any twisting. However, in the course of crystallization the two surfaces of a ribbon do not always have the same structure. In certain cases this may be caused by the adsorption of impurities on either surface. The case is the same with the ribbons deposited from any polar solvent. There could possibly also be a case in which one surface is polar, and the other, nonpolar. In these cases a surface stress would develop, leading to a twisting of the thin ribbon. Furthermore, when the molecules have an asymmetric conformation, the ribbon itself has an asymmetric structure and the surface stress acts to twist the ribbon favorably in a certain sense. Consequently, all the ribbons would twist in the same direction. In this view, twisting is considered to occur rather generally in thin ribbons. However, the surface stress decreases rapidly with an increase in the thickness, so the twisting becomes more difficult for too wide or too thick a ribbon. The analogy with a gross physical ribbon is useful in explaining the interesting electron-micrograph shown in Fig 3, which was obtained with a sample of the free D-acid from a nonanol solution. In this micrograph one can see many thin and twisted fibers split from an end of a straight and wide ribbon. Evidently twisting is likely in very thin ribbon-like fibers. However, there is a limitation in explaining the twisting phenomenon by this analogy alone. For instance, it is thereby difficult to explain why some soap fibers twist easily and others do not.

The fact that the sense of twist for the fibers of the free D(or L)-acid is opposite to that of the Li soap suggests that the sense of twist is associated with the structure of the ionic layers in crystal. The effect of the cation size was observed in a series of the alkali metal soaps. This fact suggests that the packing arrangement in the ionic layers plays an important role in determining the helical sense, but the nature of this role has yet to be determined. The solvent effect exhibited by particular alcohols is also suggestive in explaining the twisting phenomenon, since these alcohols may be involved in the formation of the soap-crystal structure and may affect the packing arrangement of molecules. Further studies are also in progress with bivalent-metal soaps, giving complicated results which will be presented in a subsequent paper.

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4) H. Wilman, *Proc. Phys. Soc.* **64A**, 329 (1951).
5) A. L. McClellan, *J. Chem. Phys.*, **32**, 1271 (1960).
6) J. D. Eshelby, *J. Appl. Phys.*, **24**, 176 (1953).
7) R. J. Bird and G. Rooney, *Nature*, **190**, 337 (1961).