

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3476—3478 (1972)

Colloidal Structure of Aluminum Soaps Dispersed in Organic Media

Yuhei UZU and Michihiro HATTORI

Chemical Institute, Faculty of Science, Shinshu University, Asahi, Matsumoto, Nagano

(Received April 19, 1972)

In connection with the structure of gels formed by metal soaps in organic media, aluminum soaps exhibit many interesting properties. Till now, the colloidal structures of many metal soaps have been widely studied by a variety of techniques. In particular, a perfect image of the soap fibers constituting the dispersed phase can be obtained by means of the electron microscope, provided that a portion of the liquid which masks the fibers is eliminated in a suitable manner.

Especially in the case of 12-hydroxystearic acid and its uni- and bivalent metal soaps, it is recognized that

the soap fibers are twisted in the form of aggregates.^{1,2)} However, no data on the trivalent metal soaps of 12 hydroxystearic acid have yet been shown, to say nothing of such a twisting structure. Its main causes seem to be its susceptibility to thermal decomposition and the difficulty of obtaining pure soaps.

To elucidate the mechanism of occurrence of such a twisting, various explanations have been proposed in the literature.^{3,4,5)} Above all, it seems reasonable to assume that the twisting is related to the conformation of the soap molecules, as has been suggested by

1) J. W. Wilson, *NLGI Spokesman*, **27**, 373 (1964).

2) T. Tachibana, K. Kayama, and H. Takeno, *This Bulletin*, **45**, 415 (1972).

3) H. Wilman, *Proc. Phys. Soc.*, **64**, 329 (1951).

4) A. L. McClellan, *J. Chem. Phys.*, **32**, 1271 (1960).

5) G. Rooney and R. J. Bird, *Nature*, **190**, 337 (1961).

Tachibana.²⁾ The present work shows that similar twisted fibers were found in the aggregates of aluminum 12-hydroxystearate dispersed in such solvents as *n*-hexadecane and white mineral oil.

Aluminum 12-hydroxystearate was prepared by an aqueous metathesis similar to the manner described for the preparation of aluminum stearate.⁶⁾ The fatty acids of the commercial products used in this work were purified by repeated recrystallization from ethanol or acetone until those of over 99% purity were obtained, as established by gas-chromatographic analysis. The acids in aqueous ethanol were treated with a slight excess of a potassium hydroxide solution at 50–60°C to yield potassium soaps. The potassium soaps were, then, heated to dissolve them in water, and a hot solution of aluminum chloride at about 90°C was added slowly until the precipitation was complete. The aluminum soaps thus obtained were filtered and thoroughly washed with distilled water and acetone to remove the residue contained in the soaps. Finally, they were dried over P_2O_5 *in vacuo* at 60°C.

The infrared absorption spectra for aluminum stearate and aluminum 12-hydroxystearate were almost identical. Moreover, a comparison of the spectra of the corresponding fatty acids with those of these aluminum soaps showed that the major distinction was the complete absence of the band at 1695 cm^{-1} due to the presence of free fatty acid in the latter, which contains little or no extractable fatty acid. In addition, the thermal analysis confirmed the absence of the transition peak of the free fatty acid. The soaps have a strong band at 983 cm^{-1} , one which is possibly due to an Al–O– covalent and coordinate type of band, as has been reported of aluminum stearate.⁶⁾ Also, two absorption bands are displayed at about 1450 and 1590 cm^{-1} which are due to the symmetric and asymmetric stretching vibrations respectively of the carboxylate group. The splitting of the latter band expected in the hydrated forms did not appear. Besides, the elementary analysis indicated that the str./Al and 12 hydroxyst./Al ratio of these soaps were about 2.0 and 1.8 respectively. On the basis of these data, the aluminum 12-hydroxystearate prepared is considered to be a mixture which consists of a disoap plus a small quantity of a monosoap.

A series of studies of the colloidal structures of these soaps has made parallel to one of the gelling properties of these soaps for various organic media. Considerable care was taken in the preparation of the specimen for examination by means of the electron microscope in order to prevent the deformation of the soap thickener structure. In order to make a specimen for electron microscopy, a small amount of the gel or gel-like precipitates was spread in a thin layer on the electron microscope's specimen grids covered with a thin film of carbon, which are then placed on a filter paper. After deoiling by wetting the paper slowly with *n*-hexane, the specimens were chromium-shadowed and examined in the electron microscope.⁷⁾ Figures 1 and

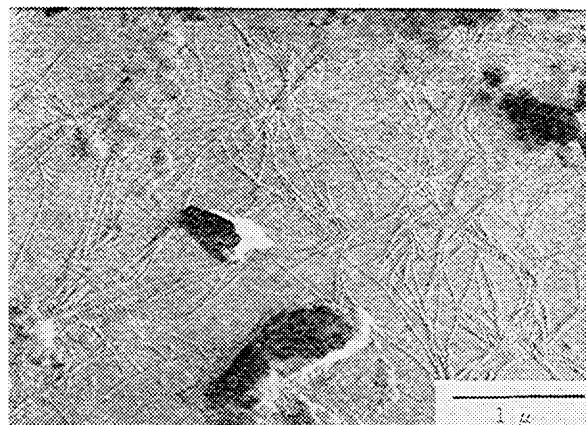


Fig. 1. Electron micrograph of twisted fiber of aluminum 12-hydroxystearate dispersed in *n*-hexadecane at 110°C.

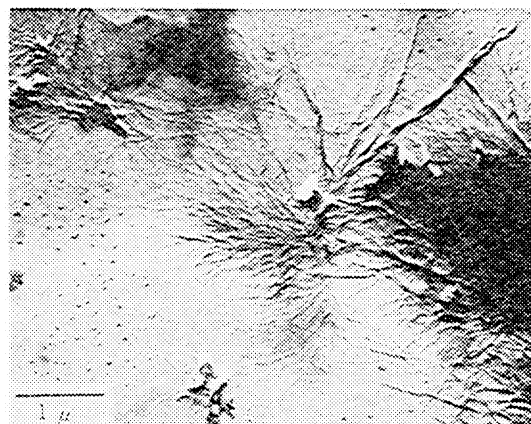


Fig. 2. Electron micrograph of aluminum 12-hydroxystearate dispersed in mineral oil at 110°C.

2 depict typical electron micrographs of fibers of aluminum 12-hydroxystearate dispersed in *n*-hexadecane and highly-refined mineral oil at 110°C. Further, the similar twisted shapes were obtained in such other organic media as amyl acetate, octyl acetate, and decyl alcohol.

Out of a fear of decomposition and a release of their free acid with a rise in the temperature, the IR spectra were examined and thermal analysis was carried out

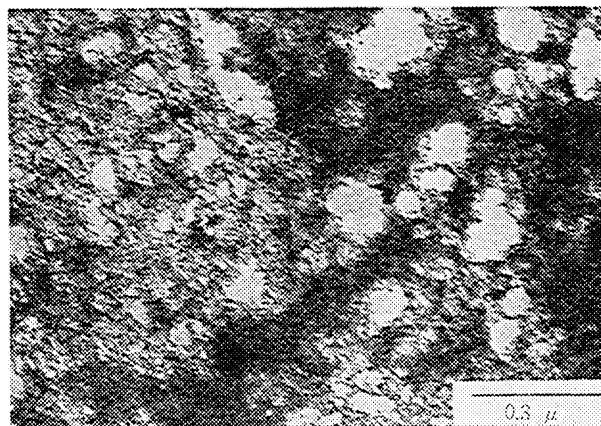


Fig. 3. Electron micrograph of aluminum stearate dispersed in mineral oil at 110°C.

6) G. H. Smith, H. H. Pomeroy, C. G. McGee, and K. J. Mysels, *J. Amer. Chem. Soc.*, **70**, 1053 (1949).

7) F. W. Anderson, R. C. Nelson, and F. F. Farley, *NLGI Spokesman*, **31**, 252 (1967).

for specimens which has been treated thermally at 90 and 110°C. There was no evidence of the release of free fatty acid as a result of the decomposition. Accordingly, it is considered probable that the twisting structure is ascribable to that of aluminum 12-hydroxystearate.

Figure 3 shows a dense honey-combed structure formed in the aggregates of aluminum stearate. It seems to indicate that such a network structure of aluminum stearate is not so easy to break as in other metal soaps in the deoiling process. This supports the view that it is due to the polymerization of aluminum

stearate, as has been reported elsewhere.⁸⁾ Furthermore, this idea may be associated, in some manner, with the abnormal low long spacing value of 40.9 Å derived from the X-ray diffraction patterns of aluminum stearate. On the other hand, the large value of 47.8 Å of the aluminum 12-hydroxystearate closely approximates the long spacing values of bivalent soaps.⁹⁾ It is suggested that these remarkable differences of the long spacing value, together with the electron-microscopic work, may be interpreted as additional evidence supporting the difference in the degree of gelatization.

8) A. E. Legar, R. L. Haines, C. E. Hubley, J. C. Hyde, and H. Sheffer, *Can. J. Chem.*, **35**, 799 (1957).

9) R. Matsuura, *Nippon Kagaku Zasshi*, **36**, 560 (1965).