Single Crystals Coimaged with the Gigantic Rod-Like Micelles in Viscoelastic Cationic Surfactant-Aromatic Additive Systems

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(Received July 22, 1988)

Synopsis. In a system of hexadecyltrimethylammonium bromide (HTAB)-salicylic acid (SA) in which a remarkable viscoelasticity is induced, we noticed the existence of single crystals coimaged with the infinitely elongated rod-like micelles. The single crystal implied the formation of a new species, a complex which resulted from the interaction of HTAB and aromatic additives.

Previously, we reported the clear detection, under an electron microscope, of gigantic rod-like micelle images in a solution of several cationic surfactants, such as HTAB and hexadecylpyridinium bromide, with some aromatic substances added.[1] These solutions were always accompanied by a remarkable viscoelasticity.[2] The gigantic rod-like micelles showed an infinite length, and they were heavily entangled with each other, like cobwebs, in the electron micrographs.[3,4] It seemed that those aspects provided a sufficient explanation of the solution behavior in all senses.

In the course of carrying out the image observation of the elongated gigantic micelles under an electron microscope, we recently became aware of the existence of a few single crystals always together with the rod-like micelles in almost all of the surfactant and aromatic additive systems. The images of these single crystals are exhibited in Fig. 1.

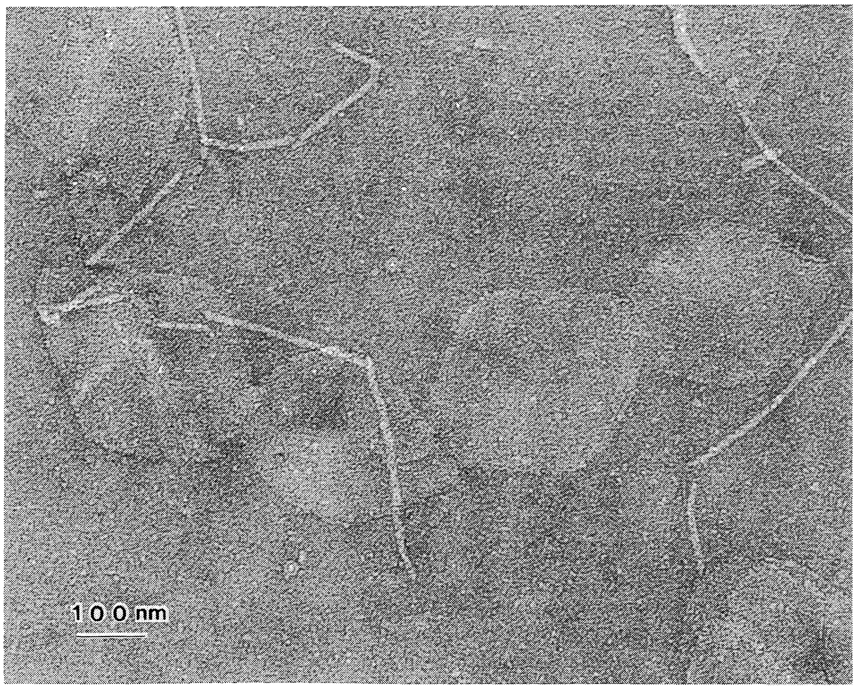
The crystals in a system of HTAB-SA typically have a well grown shape in electron micrography. The image contrast to the background suggests that the crystal thickness is nearly the same as the rod-like micelle diameter or at least of the same order.

It is obvious that the crystals found in these photos are different from those of each component, CTAB or SA, for there is a clear difference in the apparent shapes of the component crystals, excluding such cases of a plausible coming out of the crystalline materials of each component from the solutions, especially of the precipitation of the surfactants below their Krafft points.

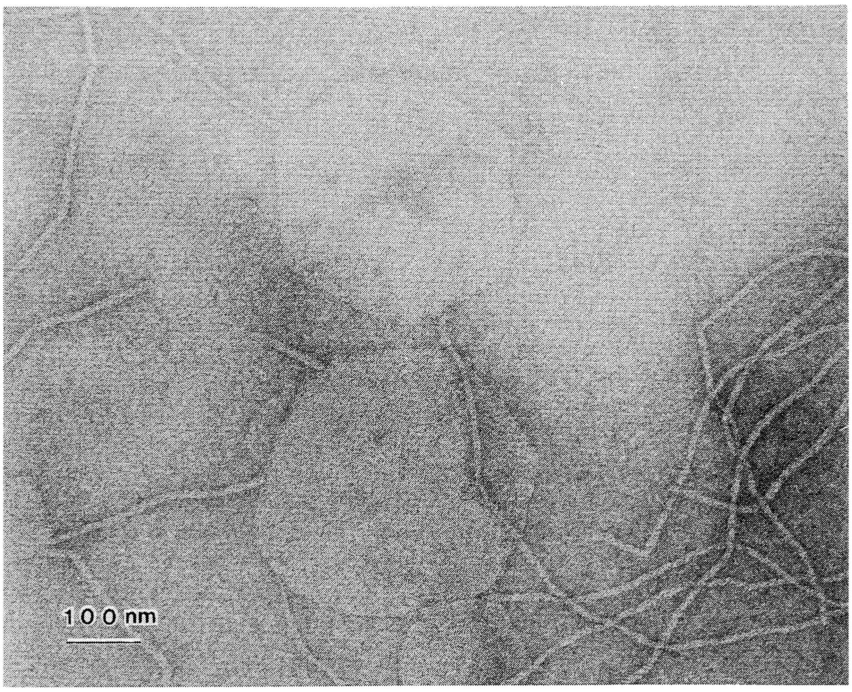
The analysis of the sharp spots caused by the electron diffraction from these single crystals are being successfully carried out in many gigantic rod-like micelle-producing systems. The spot patterns were also clearly different from those of each component crystal. The results will be reported in another place.[5]

In this context, it is worthwhile mentioning that in one of the most remarkable viscoelastic solutions, the HTAB-*o*-iodophenol system, we obtained crystalline materials which were unambiguously indicated through the elementary analysis to be composed of HTAB and *o*-iodophenol in a one-to-one molar ratio.[6] This fact distinctly reveals that a certain kind of interaction between HTAB, a quaternary ammonium, and aromatic additives acts to provide a complex.[7]

Commercially available HTAB was used after one recrystallization from an acetone-methanol mixture



(a)



(b)

Fig. 1. Single crystals coimaged in the transmission electron micrograph of CTAB–SA system in the magnification of 97,500. Specimens were prepared from 1×10^{-3} mol l^{-1} CTAB solution at mixing molar ratio of SA/CTAB=0.8. As for the details see Ref. 3.
a) Rhombus shaped single crystals are seen with a definite angle between edges.
b) Apparent hexagonal shaped single crystals are seen. The angles between edges are equal to each other as well.

while SA in a special pure grade was used as purchased. Transmission electron microscopy was carried out upon a JEOL 100CX apparatus operated at 80 kV. All the images were obtained by negative staining techniques with uranyl acetate.

We are very grateful for having received many suggestive comments on this subject from Mr. Atsuo Koreeda in the Institute of Scientific and Industrial Research of Osaka University and also for the ardent encouragement of Dr. Yoshie Kitayama of the Engineering Chemistry Department of Niigata University.

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