Effect of Alkali Metal Ions on Gel Formation in the 12-Hydroxystearic Acid/Soybean Oil System

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It has been known that 12-hydroxystearic acid (12HSA) forms a thermoreversible gel with a fibrous associated network in organic solvents. Mechanically durable gels were induced by the addition of small amounts of alkali metal ions, which can be supplied in the form of alkali metal salts of 12HSA (abbreviated as 12HS-M), even at a lower concentration range of gelling agent than with 12HSA alone. The structure of the networks was investigated by infrared spectrometry (IR), circular dichroism (CD) and scanning electron microscopy (SEM). The experiments were carried out over a total concentration range of 0.1 ≈ 4.0 wt/vol% of 12HSA and 12HS-M in soybean oil. 12HS-Na showed more effective gel forming power than any other alkali metal ions. The molar ratio of 12HSA/12HS-Na for obtaining optimal gel forming effect was 100:1. The intensity of the absorption bands of the IR spectra, due to the hydrogen-bonded hydroxyl groups, remained constant regardless of the amount of added 12HS-Na. A remarkable molar ellipticity decrease was observed with an increase in the concentration of 12HS-Na, although the maximum wavelength of the CD spectrum, originating from the chirality of 12HSA, remained constant. By SEM observation, linearly extended fibrils were observed with the addition of 12HS-Na. These results suggest that the mechanical strengthening of the gel by alkali metal ions is due to alteration of the dispersed state of the helically grown fibrous crystals of 12HSA.

KEY WORDS: Alkali metal soap, chracterization, gel, gel formation, helical aggregate, helix, 12-hydroxystearic acid, organo gel, SEM, yield strength.

In recent years, studies of the physicochemical behavior of organic polymer gels in aqueous media have progressively developed. As a consequence, relationships between network structures and the mechanical properties of the gels have been revealed for aqueous systems of many polyelectrolytes, polysaccharides and proteins. On the other hand, a large number of low-molecular weight organic substances, such as metal soaps (1–9), 12-hydroxystearic acid (12HSA) (10–14), dibenzyliden sorbitol (15), long-chain dialkyl phosphates (16), amino acid derivatives (17–21) and steroid derivatives (22–24), are also known to form network structures in various organic media. From a practical viewpoint, these substances are widely utilized as regulators for viscoelastic properties of greases and cosmetics, a solidifier for spent edible oils, and reagents for the recovery of ocean-spilled oil (18,19).

The fibrous structure of 12HSA or its metal soaps, formed in organic solvents, has been widely investigated with the aid of infrared spectroscopy (IR), X-ray diffraction, circular dichroism (CD) and scanning electron microscopy (SEM), (11,12). It is well established that the helical sense of twist is mainly affected by the chirality of molecules and the kind of metal ions or organic solvents.

Conformational changes in the helical structure of 12HSA with the addition of small amounts of alkali metal ions, were investigated to clarify the mechanical strengthening properties of the alkali metal ions.

EXPERIMENTAL PROCEDURES

Materials. D-12-HSA was purified from a commercial product according to the method of Uzu and Sugiura (13). The purity was ascertained to be more than 99% by gas chromatography. Alkali metal (Na-, K-, Cs- and Rb-) salts of 12HSA were prepared by neutralizing the purified 12HSA with the corresponding metal hydroxide in methyl alcohol. Reagent-grade soybean oil was purchased from Tokyo Kasei Co. (Tokyo, Japan) and was used without further purification.

Preparation of gels. The 12HS-M (alkali metal salts of 12HSA) powder and 12HSA powder were added simultaneously to the soybean oil, which was stored at *ca.* 90°C in advance. The mixture was then stirred until it became homogeneous and was left standing at room temperature to form a gel.

The gel stiffness was evaluated by the average penetration depth of three small steel balls (*ca.* 100 mg) placed on the center of the gel.

Evaluation of the yield strength of the gel was carried out with a FUDOH (Tokyo, Japan) Rheometer, Model NRM-2010-CW by using a disk-type adaptor with a diameter of 1.5 cm. A sliced gel (2 mm thickness) was placed on a fixed stainless-steel table and then compressed by the disk-type adaptor at a rate of 2 cm/min. The minimum stress causing a destruction of the gel was recorded.

The transparency of the gel was evaluated by light transmittance at 660 nm through a gel of 1 cm thickness in a Hitachi (Tokyo, Japan) double-beam spectrometer, Model H-600.

IR was carried out with a JEOL FT-IR (Model JTR-100; Tokyo, Japan) on a gel sample (0.2 mm thickness) supported between parallel KBr plates.

The CD of the gel was measured with a JASCO spectropolarimeter, Model J-40A (Tokyo, Japan). The measurements were carried out with a gel previously formed in a quartz cell of 1 mm at 25°C. The CD spectrum for 12HSA showed a positive peak at 294 nm. The results are expressed as molar ellipticity$[\theta]_{294}$, which is defined as

$$[\theta]_{294} = 100 \cdot \theta_{obs}/l \cdot c \qquad [1]$$

where θ_{obs} is the observed ellipticity in degrees, c is the concentration in moles per liter, and l is the length of the light path in cm.

SEM. A small portion of gel was dispersed in a mixed solvent (*n*-hexane/acetone = 8:2, vol/vol), and the dispersion was then stored overnight at room temperature. The solution containing precipitate was placed dropwise onto a clean glass plate. After drying, the residue was washed ten times with the original mixed solvents. The residues on the glass plates were coated with gold (*ca.* 300 Å), which

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was deposited by spattering of gas ions in an Eiko Ion Coater, Model IB-3 (Tokyo, Japan) at a vacuum of 0.10 $\approx$ 0.15 Torr. The samples were then observed with a JEOL Field Emission SEM, Model JSM-6300F.

RESULTS AND DISCUSSION

Gel formation. The effects of alkali metal ions on the degree of completion of 12HSA gel formation were examined. Figure 1 shows the stiffness of gels as measured by the penetration depth of steel balls into a gel with a molar ratio of 12HSA/12HS-M = 100:1. The critical gel-forming concentration (CGC) of 12HSA moved to a lower concentration range when alkali metal ions were present. The efficiency of each ion on the formation of detectable gel seems to be in the order of $\text{Na} > \text{K} \geqslant \text{Cs} > \text{Rb}$ ions. This result indicates that an alkali metal ion with a smaller diameter lowers CGS more effectively with the exception of Rb ion, which does not have any influence on the CGC of 12HSA.

The most progressive effect on the shifting among these alkali metal ions was obtained in the presence of Na ion. Figure 2 shows the strength of the gels as a function of the concentration of 12HSA, which contains 12HS-Na at various molar ratios. As shown in Figure 2, a gradual increase in the yield strength of gels at around 0.6% of 12HSA occurred, which corresponds to the results shown in Figure 1. In the presence of 12HS-Na, the gel showed a sharp increase in strength at a lower concentration region than that without 12HS-Na.

In particular, extension of the gel-forming region to the lower concentration region was observed at a molar ratio of 12HS-Na/12HSA greater than 0.25:100. When the concentration of Na ion exceeds the critical point for gel formation, the yield strength was gradually increased regardles of the molar ratio of 12HS-Na.

The turbidity of soybean oil gels increased with the addition of the alkali metal ions as shown in Figure 3. A transparent appearance was maintained until the amount of added 12HSA reached 2.5 wt/vol%. In the presence of 12HS-Na, the turbidity curves showed their bending part at lower concentrations, accompanied by a steeper decrease in clarity. Increase in the gelation temperature and the turbidity were also observed with the addition of Na ion. These results indicate that the addition of Na ion improves the crystallization of gelation and produces fairly large clusters of oil in the gel structure.

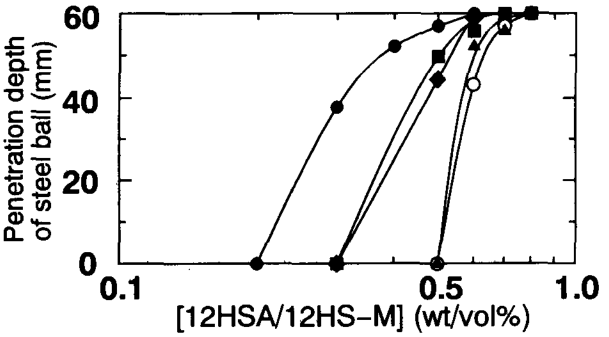

FIG. 1. Penetration depth of steel ball into gel with various kinds of alkali metal ions at a molar ratio 12-hydroxystearic acid/alkali metal salts of 12-hydroxystearic acid (12HSA/12HS-M) =100:1 soybean oil. ○, 12HSA alone; ●, M = Na; ■, M = K; ▲, M = Rb; ◆, M = Cs.

Function of hydrogen bonding in gel formation. To clarify the mechanism for the enhancement of gelation by the addition of 12HS-Na, IR measurements were carried out to estimate the extent of intermolecular hydrogen bonding among 12HSA molecules. Figure 4A shows the IR spectra of 12HSA/soybean oil gels in a higher wavenumber region. The absorbance at 3200 cm^{-1}, known to be derived from hydrogen bonding (9), increased linearly with the increase in the amount of 12HSA. Figure 4B

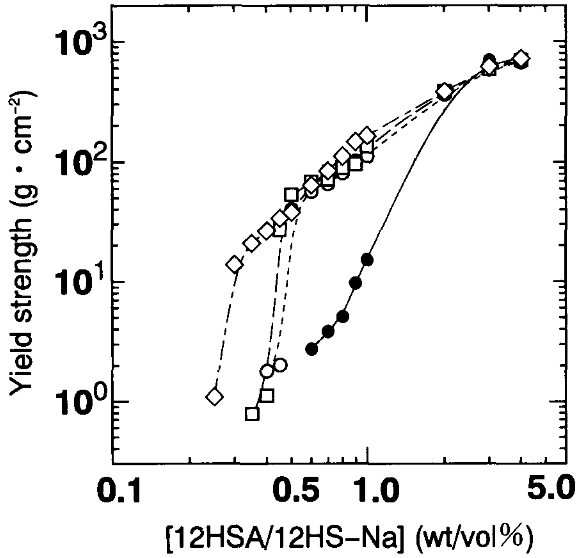

FIG. 2. Change in the yield strength of soybean oil gel with addition of 12HSA that contains various molar ratios of 12HS-Na. 12HSA/12HS-Na molar ratio: ●, 100:0; ○, 100:0.25; □, 100:0.5; ◇, 100:1.0. Abbreviations as in Figure 1.

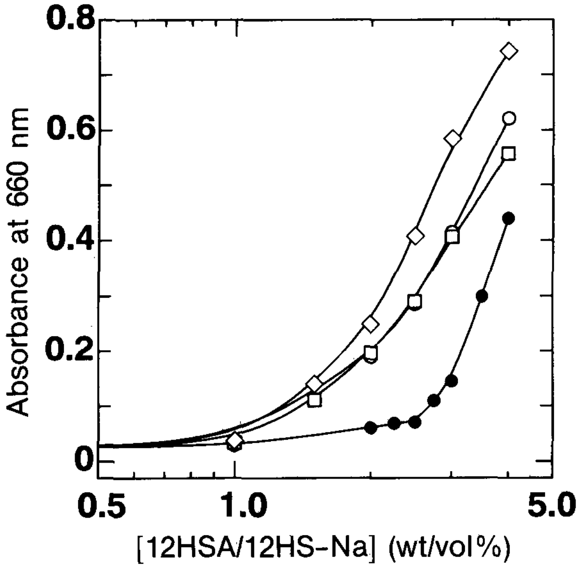

FIG. 3. Increase in the absorbance at 660 nm of soybean oil gel with addition of 12HSA that contains various molar ratios of 12HS-Na. 12HSA/12HS-Na molar ratio: ●, 100:0; ○, 100:0.25; □, 100:0.5; ◇, 100:1.0. See Figure 1 for abbreviations.

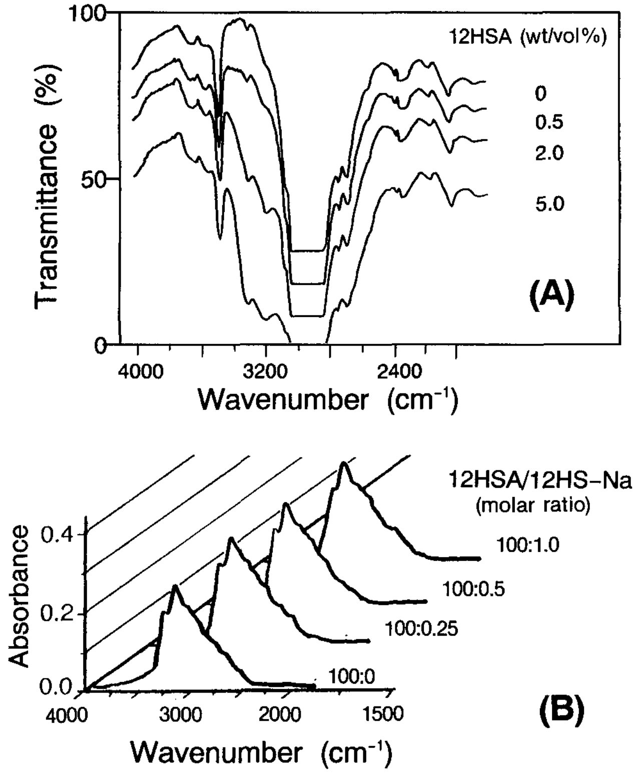

FIG. 4. Infrared (IR) spectra of 12HSA in soybean oil gel (A); subtracted IR spectra of 12HSA (1.0 wt/vol%)/12HS-Na/soybean oil gel (B). See Figure 1 for abbreviations.

shows the effect of 12HS-Na on the subtracted absorption spectra between the sample and pure soybean oil. No alteration was observed in each spectrum, indicating the maintenance of a certain amount of hydrogen bonding. These results show that the enhancement of gel formation by the addition of Na ion would not be caused by any alteration of the state of hydrogen bonding.

Evaluation of the degree of helical structure formation. Figure 5 shows the variation in the molar ellipticity of 12HSA in soybean oil gels as a function of 12HS-Na concentration. Molar ellipticity at 294 nm originates from an associated state among the carboxylic acid groups near the chiral hydroxyl group.

The CD spectrum of fibrous crystals of D-12HSA alone showed a large positive peak, indicating formation of a left-handed twist. $[\theta]_{294}$ Showed a slight decrease with the addition of 12HSA. Addition of 12HS-Na resulted in a decrease in the intensity of $[\theta]_{294}$, which had a minimum at a total concentration around 2 to 2.5 wt/vol%. This decrease was enhanced by an increase in the molar fraction of 12HS-Na. At the same time, the ellipticity at the minimum showed an inversion from positive to negative. This suggests either disorder of the chiral helical structure or the coexistence of a helical counter twist in the 12HSA crystals.

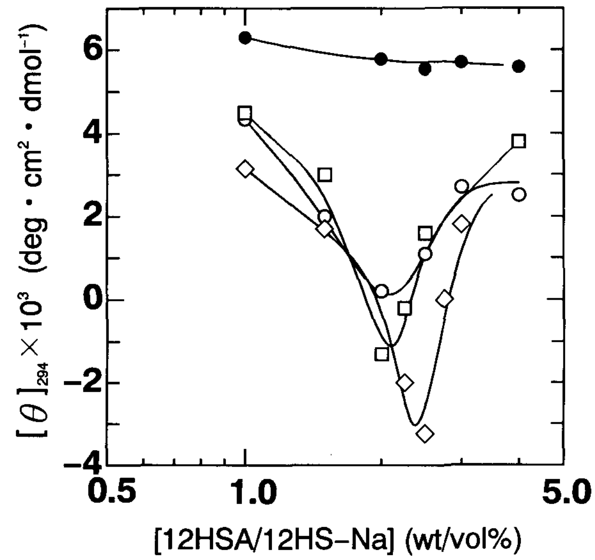

FIG. 5. Change in the molar ellipticity of soybean oil gel at 294 nm with addition of 12HSA that contains various molar ratios of 12HS-Na. 12HSA/12HS-Na molar ratio: ●, 100:0; ○, 100:0.25; □, 100:0.5; ◇, 100:1.0. See Figure 1 for abbreviations.

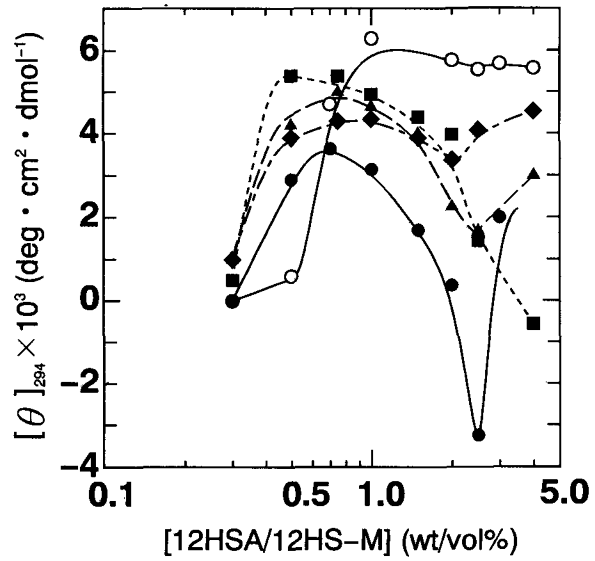

FIG. 6. Change in the molar ellipticity of soybean oil gel at 294 nm with the addition of 12HSA that contains various kinds of 12HS-M at the molar ratio 12HSA/12HS-M = 100:1. ○, 12HSA alone; ●, M = K; ▲, M = Rb; ◆, M = Cs. See Figure 1 for abbreviations.

Figure 6 shows the molar ellipticity of 12HSA in soybean oil gels as a function of the total concentration of 12HSA in the presence of various kinds of alkali metal ions. In each system, the positive molar ellipticity was obviously observed even below the CGC. The CD spectrum showed, however, a decrease in the intensity in the concentration range of 12HSA above 1 wt/vol%, accompanied by a sharp minimum in the concentration range from 2 to 3 wt/vol%, with the exception of K ion. Furthermore, the inversion from positive to negative was also observed for the 12HSA/12HS-K system.

SEM observation. The effects of sodium soap on the helical structure of 12HSA were observed by SEM. Figure 7 shows microscopic photographs of typical fibrous structures of 12HSA with and without alkali metal ions. There seems to be an obvious difference between these pictures.

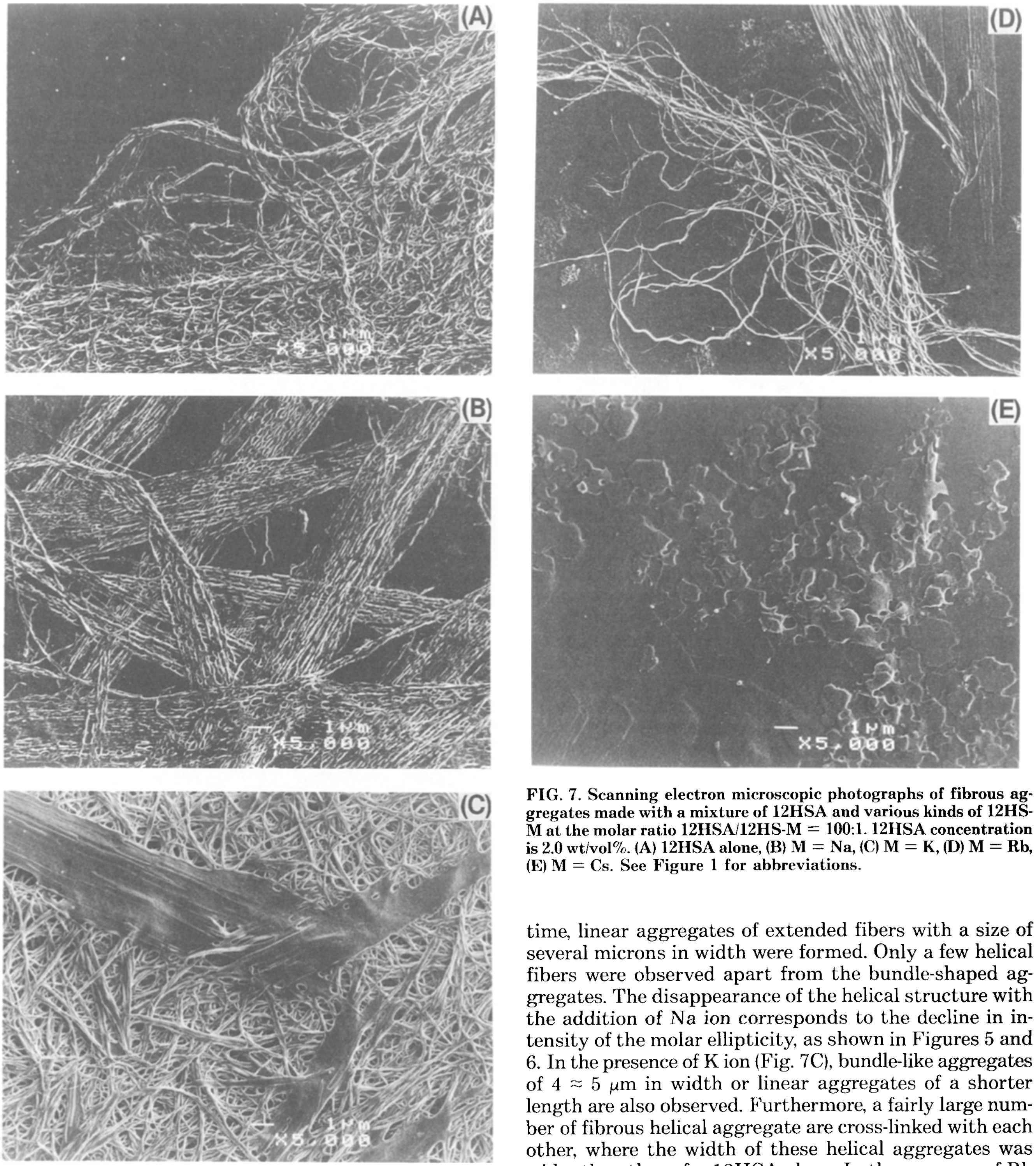

FIG. 7. Scanning electron microscopic photographs of fibrous aggregates made with a mixture of 12HSA and various kinds of 12HS-M at the molar ratio 12HSA/12HS-M = 100:1. 12HSA concentration is 2.0 wt/vol%. (A) 12HSA alone, (B) M = Na, (C) M = K, (D) M = Rb, (E) M = Cs. See Figure 1 for abbreviations.

In the case of 12HSA alone (Fig. 7A), the network structure is made up of a large number of individual fibers randomly entangled with each other. 12HSA forms a twisted fiber of 0.01–0.1 μm in width. These fibers also elongate progressively in soybean oil media, and each fibril has a few junctions. In the presence of Na ion (Fig. 7B), most of the helical structure disappeared. At the same time, linear aggregates of extended fibers with a size of several microns in width were formed. Only a few helical fibers were observed apart from the bundle-shaped aggregates. The disappearance of the helical structure with the addition of Na ion corresponds to the decline in intensity of the molar ellipticity, as shown in Figures 5 and 6. In the presence of K ion (Fig. 7C), bundle-like aggregates of 4 ≈ 5 μm in width or linear aggregates of a shorter length are also observed. Furthermore, a fairly large number of fibrous helical aggregate are cross-linked with each other, where the width of these helical aggregates was wider than those for 12HSA alone. In the presence of Rb ion (Fig. 7D), both linearly growing bundle-like aggregates and helical ones are present simultaneously, indicating the inhomogenity of the aggregate. This result suggests that each aggregate was dispersed independently compared to that for the system of Na or K ions. In the presence of Ce ion (Fig. 7E), only polyhedral crystals were found, which may consist of cesium soap. As shown in Figure 6, helical aggregates seem to remain sufficiently in this system. This may suggest that the helical part of these crystals preferentially dissolves into the oil phase, because the inhomogenity of the structure would be increased in this system.

The sense of twist for many metal salts of 12HSA in organic solvents was studied from SEM observations by Tachibana *et al.* (6–8). It has been well established that only a left-handed helical aggregate is formed for 12HSA, 12HS-Rb and 12HS-Cs in Nujol, whereas both left-handed and right-handed aggregates coexist with 12HS-Na and 12HS-K. This suggests that the probability of observing right-handed aggregates would increase with the decrease in the diameter of the alkali metal ion. Therefore, the remarkable decrease in molecular ellipticity for both 12HS-Na and 12HS-K systems may reflect the relative difference in the contribution to their sense of helix. The probability of formation of a reversed helical aggregate due to the presence of alklai metal salts that have metal ions with a small diameter may prevent the formation of well-extended helical aggregates for 12HSA and thus form widely and linearly extended aggregates. Because these bundle-shape aggregates induce the formation of a network with a three-dimensional framework, soybean oil would be maintained within these fibrous aggregates more effectively than in the 12HSA system. Sodium ion is much more effective than other alkali metal ions for producing linear aggregates or decreasing the CGC. On the other hand, the influence of other ions on the formation of the helical structure of 12HSA is negligible, because the fibrils of 12HS-Rb and 12HS-Cs tend to form a left-handed twist. However, every alkali metal ion used in this work may prevent the formation of a left-handed helical aggregate; and in fact, the decrease in the molar ellipticity tends to decrease with the order of the atomic number.

The main conclusions to be drawn from these results are as follows. The gel region of 12HSA in soybean oil was expanded to a lower concentration region with the addition of small amounts of alkali metal ions. Because the IR spectra indicated that the intensity of absorption due to hydrogen bonding remained constant independent of the added amount of alkali metal ions, the total amount of 12HSA responsible for gel formation was unchanged. A remarkable molar ellipticity decrease was observed for the gels with addition of alkali metal soaps, indicating the disappearance of helical aggregates. This decrease may be attributable to the opposite sense of twist originating from the alkali metal soaps. The formation of a novel gel is due to transformation of the helical sense of 12HSA into a linearly extended state with the addition of alkali metal ions.

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