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Flocculation of Sodium Bis(2-ethylhexyl) sulfosuccinate Reversed Micelles in Isooctane

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The observation of reversed micelle in AOT[sodium bis(2-ethylhexyl) sulfosuccinate] /isooctane solution was carried out by a freeze-fracture transmission electron microscope. The micrograph of 5w/v% AOT/isooctane solution at R=1 ([H_2O]/[AOT]) showed that the microparticles of reversed micelles with the size less than 10 nm existed individually and they were scarcely changed by dilution with isooctane.

On the other hand, the micrograph of 5%w/v AOT solution at R=20 was greatly different from that at R=1. Large particles with size less than 200 nm were observed. They appeared to be flocs of reversed micelles which flocculated loosely. The flocculation was also confirmed by a cryo-transmission electron microscope (cryo-TEM). The extent of the flocculation was decreased by dilution of the AOT solution at R=20 with isooctane. This phenomenon was supported by measuring T_1 of solubilized water with ^{1}H-NMR spectroscopy.

It is concluded that the AOT reversed micelles were observed visually and the flocculation of AOT reversed micelles was directly proved. It was confirmed that the flocculation occurred easily in higher AOT and water concentrations before percolation occurred. © 1997 Elsevier Science B.V.

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1. Introduction

Reversed micelles which are formed in apolar solvent by surfactants can solubilize water more or less. The water in reversed micelles is localized in the interior of the reverse micelles, forming a small water pool. The interior water pool is polar, and the exterior solvent is apolar. This is considered as a microcompartmentalised system, which has been recently of great interest to researchers. For example, Luisi et al. built self-replicating bounded structures in relation to autopoiesis by using reversed micelles[1,2].

Reversed micelles, which is easily formed in an apolar organic solvent by sodium bis(2-ethylhexyl)sulfosuccinate(AOT), can solubilize a relatively large content of water in the micellar core. Hence, the physical properties of AOT reversed micelles have been studied by many researchers. The molar ratio of water to surfactant, R is a key parameter which affects significantly the physical properties of AOT reversed micelles. As R increases, the sizes of reversed micelles as well as water pools increase, keeping a spherical shape. Almost all water in water pools below R=10 is hydrated to AOT polar head groups and counter ions, but further addition of water leads to the appearance of free water in the core of water pool[3-5]. On the other hand, we recently reported by NMR spectroscopy[6] that the property and structure of the AOT reversed micelles below R=2 are remarkably different from those of the spherical reversed micelles above R=10 and the mobility of water below R=2 is significantly suppressed. It is well known that percolation occurs at high surfactant concentrations: It is assumed by light scattering[7,8] that the interaction of reversed micelles in oil occurs usually more or less, leading frequently to fusions, at relatively low concentration of surfactant. Therefore, it is of interest to observe visually the AOT reversed micelles.

In this work, the observation of AOT reversed micelles in isooctane was carried out by a freeze-fracture transmission electron microscopy (freeze-fracture TEM) and by a cryo-transmission electron microscopy(cryo-TEM). It was reported that the water in oil (W/O) microemulsion of the D_2O-n-dodecane-AOT was observed by a freeze-fracture-TEM[9], but the AOT reversed micellar solution containing a relatively low content of water has never been investigated by a direct visualization technique such as cryo-TEM so far as we know. Therefore, this observation should give new insight into a static structure of AOT reversed micellar system. In this paper, the AOT reversed micellar structure in isooctane was discussed in relation to flocculation of reversed micelles.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl)sulfosuccinate(AOT) was a commercial product from Sigma. Isooctane (Cica-merck for spectroscopy) was distilled. Water was

redistilled. Octane-d_{18} and water-^{17}O(10.1%^{17}O) were purchased from A Matheson Comp. and CEA-ORIS, respectively. The AOT solutions were prepared by dissolving AOT and water in isooctane at room temperature.

2.2. Electronmicroscopy

The freeze-fracture replica film was prepared on a Balzers BAF 400 freeze-fracture device. An aliquot of AOT reversed micellar solution on a sample stage was vitrified in cooled liquid nitrogen. Under reduced pressure, the vitrified specimen was fractured at -130℃, and the fractured surface was shadowed by platinum at an elevation angle of 45° and deposited by carbon at 90 ° [10]. The replica film was washed with ethanol /water mixture.

Cryo-TEM specimen preparation was carried out according to a procedure described in the literature[11]. A filmy drop of AOT solution on an electron microscope grid was vitrified by jet-freezing in cooled liquid nitrogen[12]. The grid with the vitrified specimen was mounted on a Hitachi 5001-C cold stage and observed in TEM under liquid N_2 cooling. Freeze-fracture TEM and cryo-TEM were observed on a Hitachi H-800 electron microscope at 100 kV.

2.3. NMR Measurements

The AOT solution was dissolved in 10%v/v octane-d_{18} in isooctane solution. NMR spectra were measured at 500 MHz(^1H) with a JEOL JMN-GSX 500 spectrometer at 27 ±0.2℃, as described in the previous paper[6]. The longitudinal relaxation(T_1) of proton of water was measured by the standard inversion recovery method.

3. Results and Discussion

Reversed micelles as well as normal micelles are very highly dynamic structures. They collide and after a couple of milliseconds they separate again into single micelles. In addition, the micelles are in rapid equilibrium with surfactant monomers. It is assumed that a freeze-fracture TEM would show probably the real picture of a reversed micellar solution because a freeze-fracture replica film of the reversed micellar solution is made by rapid cooling to -150 ℃ to stop the dynamic nature of the structure instantly.

Figure 1a shows an electron micrograph of an AOT reversed micellar solution (5% w/v AOT-isooctane solution, R=1). The microparticles of reversed micelles at R=1 were observed individually, and the images were not changed by dilution of the AOT solution with isooctane from 5%w/vAOT to 1%w/vAOT. It was reported by light scattering method[13] that the hydrodynamic diameter of the micelles below R=2 was approximately 4nm. Although Fig.1a showed that the microparticles with their size less than 10nm were observed, a more accurate estimate of the size could not be done. Visual observation by a freeze-fracture TEM indicated that the

reversed micelles at R=1 were spheroidal and the particles existed individually. This is not incompatible with our result of NMR spectroscopy in the previous paper[6] that the AOT aggregate below R=2 is rigid and compact.

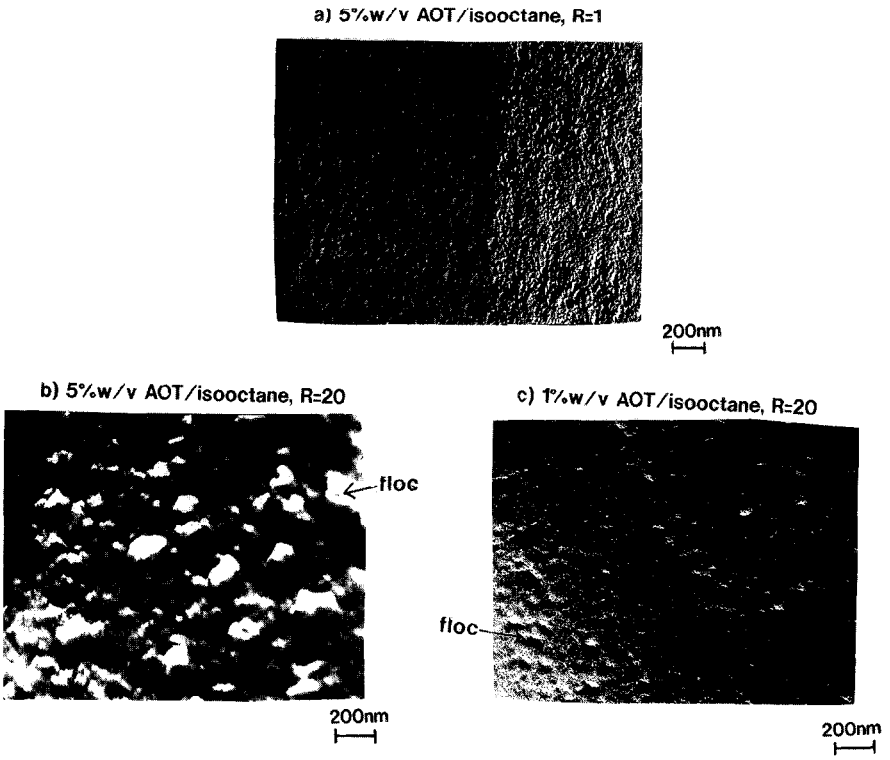

Figure 1. Freeze-fracture transmission electron micrographs of AOT reversed micelles.

It was reported that, as R increases, the sizes of AOT reversed micelles increased[14,15]. The water pool at R=20 contains free [3,6]. Figure 1b shows the images of 5%w/v AOT/isooctane solution at R=20. Small particles with their sizes less than 20nm were observed in the overall picture. They should correspond to the reversed micelles at R=20 because the size was reported to be ca.15nm by light scattering[13]. Besides small particles, large particles with various sizes less than 200nm were observed at the same time. The large particles are nonspherical shape and appeared to be a floc of reversed micelles. The image at R=20 suggested that the small reversed micelles assembled each other to form flocs in 5%w/vAOT

solution. Flocs are sometimes called clusters. The flocculation, which means the formation of loose aggregates of reversed micelles, different from percolation. It is well known that percolation occurs in higher AOT and water concentrations[16-18]. Percolation means the formation of more rigid and larger aggregates or network structure of reversed micellar solutions, often accompanied by phase separation.

Manabe et al. [19] reported by the measurement of electric conductivity that, as AOT and water increased, the interaction of AOT reversed micelles led to the formation of clusters before threshold of the percolation. Hasegawa et al. [20] assumed by utilizing the excitation energy transfer phenomenon that AOT reversed micelles were not randomly dispersed in isolate state, and interacted each other to form a cluster at 0.2M and R=30. Therefore, our results support that the flocculation occurs before percolation does.

In the image of 1%w/vAOT solution at R=20(Fig.1c), the small reversed micelles with various sizes of 10-20nm were observed in the overall picture. On the other hand, the flocculation of reversed micelles was significantly decreased and the size of flocks was small.

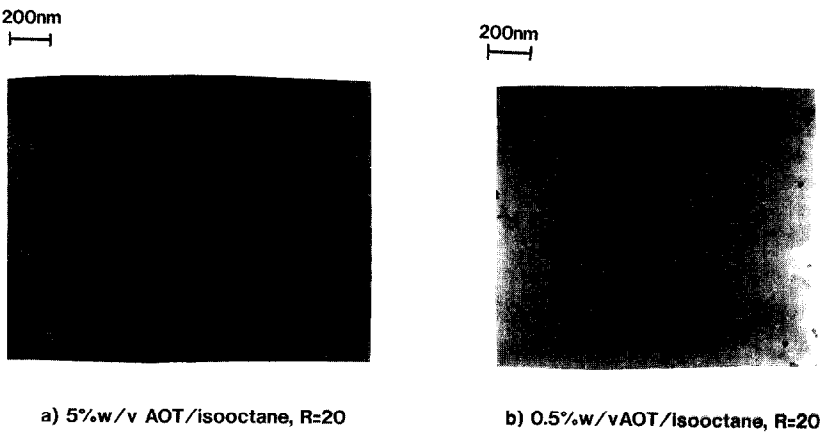

Figure 2. Cryo transmission electron micrographs of AOT reversed micelles.

The size of freeze-fracture replica images tends to be larger than the real one. Therefore, we tried to confirm the flocculation of AOT reversed micelles at R=20 by cryo-TEM, which is a direct visualization method of vitrified specimens, as a technique for avoiding some artifacts that hinder TEM observation. This technique was applied to an aqueous micellar solution which is in dynamic state[11], and furthermore TEM images of molecular assemblies were correlated with the rheological behaviours[10,21]. Imae demonstrated by Cryo-TEM that the viscoelastic solution of sodium alginate and poly(ethylene oxide) forms a super-

network structure by Cryo-TEM[12].

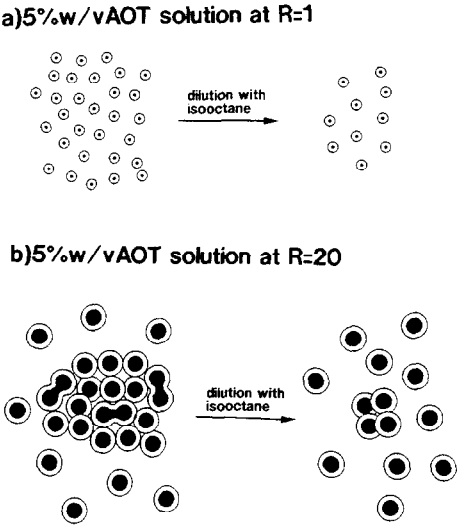

Figure 3. Schematic illustration of flocculation of AOT reversed micelles.

Figure 2a and 2b show Cryo-TEM photographs of 5%w/v and 0.5%w/vAOT - isooctane solutions at R=20, respectively. The Cryo-TEM images supported that the flocculation of AOT reversed micelles occurred at R=20 and was more promoted in higher concentration of AOT. The Cryo-TEM images of isolated micelles were not distinguished. It may be due to a small difference between the electron densities in the micellar interface. The addition of metallic ions such as Co^{2+} ion and tungstphosphorate ion which would be expected to elevate a difference of their electron densities in the micellar interface, but such effects were not observed.

The results of TEM observation are illustrated in Fig.3. The flocculation occurred at 5%w/v AOT solution and R=20. However, the dilution of the AOT solution with isooctane decreased the extent of flocculation. On the other hand, any flocculation did not occur at R=1, independent of AOT concentration. It is of interest that such a flocculation is characteristic of reversed ionic micelles, because flocs of normal(aqueous) ionic micelles are not observed due to a mutual repulsion between electric charges of normal ionic micelles.

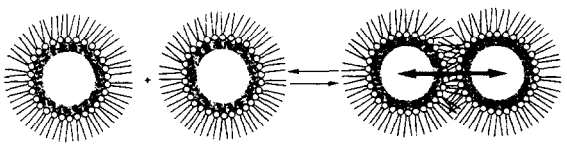

Figure 4. Schematic illustration of collision of AOT reversed micelles.
Graish part in a water pool; hydration water :
White part in a water pool; free water

When a collision of droplets occurs, as shown in Fig.4, it is assumed that the surfactant layer separating water cores of contiguous droplets is opened and water molecules migrates each other, resulting change in the area and property of hydration layer. This suggests that the ratio of bound water to free water may be changed. According to a two state model[22], the longitudinal relaxation time(T_{1obs}) of ^1H -NMR of the solubilized water may be given by

$1/T_{1obs} = 1/T_{1f}\, f_f + 1/T_{1b}\, f_b$ (1)

where T_{1f} and T_{1b} are the longitudinal relaxation times of free and bound water, respectively, and f_f and f_b are fractions of free and bound water, respectively. Figure 5 shows the plots of T_{1obs} of solubilized water in AOT reversed micelles of R=10 and 20 against concentration of AOT. The values of T_{1obs} decreased gradually with concentration of AOT at R=20, but those of R=10 changed hardly with decreasing concentration of AOT. It was confirmed visually that the flocculation is apt to occur with increase of AOT concentration at R=20. The water pools at R= 20 contain free water as well as bound water, in which the ratio of f_f to f_b is near to 1[6]. Therefore, the increase of the T_{1obs} with AOT concentration at R=20 suggested that the property of hydration layer was changed by flocculation, resulting in increase of the ratio of f_f to f_b. This effect is assumed to bring about increase of T_{1obs} for the solubilized water according to eq.[1]. On the other hand, the result at R=10 does not mean that the flocculation occur scarcely because the water pool below R=10 is occupied overwhelmingly by bound water and f_b may be unity. However, it is assumed that the solubilized water plays an important role as adhesive agent in the process of flocculation. The NMR result was in any event not incompatible with the flocculation at R=20.

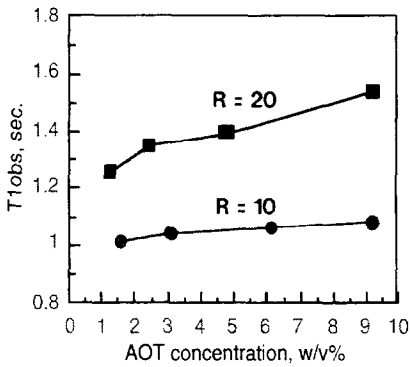

Figure 5. 1H-NMR relaxation time, T_1 of solubilized water in AOT-isooctane-d-octane solution at 27℃ as a function of concentration of AOT.

In this study, the AOT reversed micelles were observed visually for the first time and the flocculation of AOT reversed micelles was directly proved. It was confirmed that the flocculation occurred easily in higher AOT and water concentrations before percolation occurred.

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