

Structural Change of Emulsions in Forming of Metal Colloids in the Emulsions

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Introduction

Synthesis and assembly of metal nanoparticles of well-defined size and geometry is one of the significant subjects in advanced nanotechnology. Reverse micelles are thermodynamically stable mixtures of water, oil, and surfactant where the water domains are separated from oil by a monolayer of surfactants. In the synthesis of metallic nanoparticles, the size and shape of metallic nanoparticles can be controlled by the shape of water domain as well as intermicellar potential, and particularly either functionalized surfactants (i.e. the counterion of the surfactant is one of the reactants) or mixed surfactants can be used as templates to assemble nanoparticles into well-defined two- and three-dimensional spatial organizations. Silver colloidal particles are known to be synthesized by photo-reduction of AgNO₃ in the reverse micellar systems for surfactants/oil/water including Ag⁺ [1]. In the photo-reduction process, we attempt to characterize the structure of isolated and aggregated metal nanoparticles [2] in various reverse micellar systems, and estimate the change of average size of water domain (water droplet) including silver nanoparticles during the reduction by means of small angle X-ray scattering (SAXS).

Experimental

Silver colloidal dispersion (11 mM) was prepared from AgNO₃ solution by the irradiation of 500W high-pressure Hg-lamp. This AgNO₃ solution was composed of 8.3 vol% distilled water, 41.7 vol% petroleum solvent (main compounds: paraffin > 90%, naphthen < 10%), and 50 vol% surfactants. The mixture of distilled water and petroleum solvent contained Ag⁺ and two surfactants [cationic surfactant (A) and nonionic surfactant (B - F)], as shown in Table 1. The volume ratio of cationic to nonionic surfactant was 5 to 1. All the surfactants were kindly provided from Nikka Co. Ltd. The obtained samples were then poured into cells sealed with Kapton film for SAXS measurements. The measurements were performed at BL-15A. The scattering data was collected by the position sensitive proportional counter (PSPC).

Results and Discussion

Figure 1(a) shows SAXS profiles (log I(q) vs. q) of Ag⁺ solutions (before reduction) prepared in the mixture of water and petroleum solvent, containing two kinds of

surfactants, i.e., cationic and nonionic ones. Here q is the magnitude of the scattering vector, defined as $q = (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle and λ is the wavelength of X-ray. The maximum intensity appears around $q = 1.13 \text{ nm}^{-1}$ (cationic A + nonionic B) and $q = 0.71 \text{ nm}^{-1}$ (cationic A + nonionic F), respectively. The maximum peak position depends on the length of polyoxyethylene chains in the nonionic surfactant molecule. Figure 1(b) shows SAXS profiles of the cationic A solution as well as the mixed solution (cationic A + nonionic E) with and without Ag⁺ (before reduction) in the mixture of water and petroleum solvent. This figure indicates that the addition of nonionic surfactant to the cationic surfactant solution leads to change the size of reverse micelles, which reflect the size of water droplet. At a small q range ($q < 0.5 \text{ nm}^{-1}$), the scattered intensity of solution with Ag⁺ is much stronger than that of solution without Ag⁺. Thus the Ag ions enhance the scattered intensity without changing the size of water droplet. The investigation for the change of water droplet in forming of Ag nanoparticles during photo-reduction is in progress.

Table 1. Surfactants used in this experiment

Surfactant	Molecular formula
Cationic A	(C ₁₈ H ₃₇) ₂ CH ₃ -N ⁺ -CH ₂ CH ₂ OH X ⁻
Nonionic B	C ₁₂ H ₂₅ -O-(CH ₂ -CH ₂ -O) ₃ -H
Nonionic C	C ₁₂ H ₂₅ -O-(CH ₂ -CH ₂ -O) ₅ -H
Nonionic D	C ₁₂ H ₂₅ -O-(CH ₂ -CH ₂ -O) ₇ -H
Nonionic E	C ₁₂ H ₂₅ -O-(CH ₂ -CH ₂ -O) ₉ -H
Nonionic F	C ₁₂ H ₂₅ -O-(CH ₂ -CH ₂ -O) ₁₅ -H

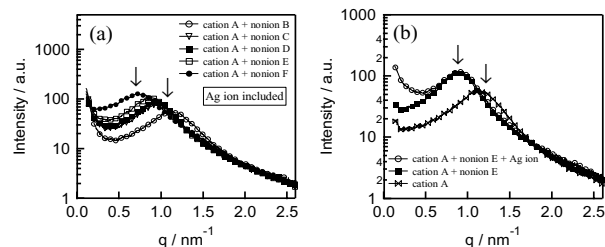


Fig. 1. SAXS profiles obtained from (a) Ag⁺ solutions containing both cationic A and nonionic (B - F) surfactants, and (b) solution of A, mixed surfactant solution (A+E) with and without Ag⁺ before photo-reduction.

References

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