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

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Introduction

Surfactants are known to have the function to solubilize hydrophilic substances in organic solvents. The method to synthesize colloidal metal nanoparticles in the hydrophilic domain produced by the reverse micelles of surfactants is very important for the purpose of control of the size and dispersity of metal nanoparticles [1]. Silver colloidal particles can be synthesized by photo-reduction of $AgNO_3$ in the reverse micellar systems for surfactants/oil/water [2]. The aim of this study is to determine the solvation structure of Ag^+ and Br^- in the reverse micelles of various surfactants in oil/water systems, and to pursue the change of solvation structure in the photo-reduction process of AgBr. In this report, we demonstrate the result of EXAFS analysis for the solvation structure of Br^- in the reverse micellar systems.

Experimental

NaBr solutions (455 mM) were composed of 9.0 vol% distilled water, 45.5 vol% petroleum solvent (main compounds: paraffin > 90%, naphthen < 10%), and 45.5 vol% cationic surfactant (A - C), as shown in Table 1.

Other Br^- (333 mM) solutions dissolving more than two kinds of surfactants were composed of 8.3 vol% distilled water, 41.7 vol% petroleum solvent, and 50 vol% surfactants. These solutions contained both Br^- and surfactants [cationic surfactant (A), nonionic surfactant, and DTAB (or TBAB)], 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. Those samples were then poured into cells for EXAFS measurements.

Br-K edge EXAFS spectra were collected at the BL-7C and/or BL-10B. The EXAFS measurements were carried out at room temperature in a transmission mode to estimate the coordination numbers around Br^- in the water domain in the reverse micellar systems.

Results and Discussion

Figure 1(a) shows the Br-K edge EXAFS Fourier transforms for 455 mM NaBr solutions in reverse micelle of cationic surfactant (A - C), comparing with that for 500 mM NaBr aqueous solution. Due to the addition of cationic surfactants, the height of main peak assigned to Br-O and/or Br-C bond decreases. Especially, in the case of cationic C, the decrease is remarkably observed owing to the decreasing contributions of hydrated bromide ions, which is different from the cases of cationic A and B.

Figure 1(b) shows the Br-K edge EXAFS Fourier transforms for 333 mM Br^- solutions in the mixed reverse micelle of cationic A and nonionic surfactants with and without Ag^+. In the cases of the addition of DTAB or TBAB instead of NaBr, the height of main peak decreases. It is suggested that DTAB or TBAB have a great influence on the decreasing hydration of bromide ions in the water domain, because these exist in the boundary of oil/water.

On the other hand, the addition of Ag^+ leads an increase of the height of main peak. This indicates the interaction between Ag^+ and Br^- might be caused by the crystalization. The detailed analysis is in progress.

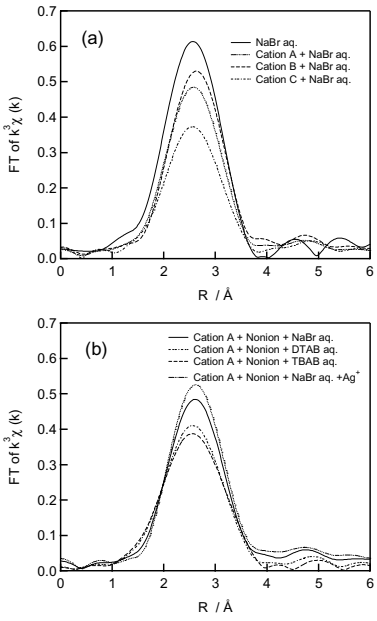

Fig.1 Fourier transforms of Br-K edge for (a) cationic solutions containing Br^-, and (b) the mixture of cationic and nonionic ones containing Br^-.

Table 1. Surfactants used in this experiment

Surfactant	Molecular formula
Cationic A	$(C_{18}H_{35})_2CH_3$-N^+-CH_2CH_2OH X^-
Cationic B	$C_{18}H_{37}(CH_3)_2$-N^+-CH_2CH_2OH X^-
Cationic C	$C_{12}H_{25}(CH_3)_2$-N^+-CH_2-C_6H_5 X^-
Nonionic	$C_{12}H_{25}$-O-$(CH_2$-CH_2-$O)_9$-H
DTAB	$C_{12}H_{25}(CH_3)_3$-N^+ Br^-
TBAB	$(C_4H_9)_4$-N^+ Br^-

References

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