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Hydration Structure of Metal Ions Restricted in Reverse Micelle of AOT

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Introduction

An extended X-ray absorption fine structure (EXAFS) technique is quite effective to determine the local structure around a target atom or ion. Then we applied EXAFS technique to study nano-scale RbBr solution, which we named RbBr nanosolution (NSN), confined in the slit-shaped hydrophobic nanospace of activated carbon fiber (ACF), showing hydration anomalies in the preceding papers [1, 2]. Also, NSNs formed in water nanodroplet surrounded by amphiphilic molecules have physically and chemically unique properties because of the size effect of water droplet. An explicit anomaly of hydration structure for Cu ion dispersed in water droplet restricted in reverse micelle of dioctyl sulfosuccinate sodium salt (aerosol OT; AOT) is described in this report.

Experimental

We synthesized $Cu(AOT)_2$ sample from $Cu(NO_3)_2$ and highly purified AOT (>98%; Aldrich). Also, we can control the diameter of inner water phase formed by AOT by adjusting the water content (here, concentrated aqueous solution of $CuSO_4$) against the concentration of AOT. Here, we denote the water content as *w*. The reverse micelles of $Cu(AOT)_2$ having different diameters for water phase were obtained in heptane as an oil phase. These samples were sealed in glass cell with Kapton film. All EXAFS spectra for Cu K-edge (89801.3 eV) were recorded at BL-10B of Photon Factory, High Energy Accelerator Research Organization in Tsukuba.

Results and Discussion

We used three kinds of NSN samples and the mean diameters for the reverse micelles determined by the dynamic light scattering method were 3.5, 4.5, and 7.3 nm for *w*=2, 4, and 10, respectively. Figure 1 and Table 1 show the Fourier transform of EXAFS oscillation for Cu K-edge of NSNs and bulk solution and analytical results of curve fitting for these samples, respectively. The results indicated that a mean hydration number and distance between a Cu ion and an oxygen atom of a water molecule for the nanosolution are 2.4±0.3 and 0.197±0.003 nm, respectively. Here, the hydration number for NSN is less than that of bulk phase, while the distance between a Cu ion and a water molecule is similar to that of bulk solution. These results strongly indicate that such a hydration structure around Cu ion in reverse micelle is strongly affected by the restriction effect, especially the geometrical restriction from the pore wall of AOT.

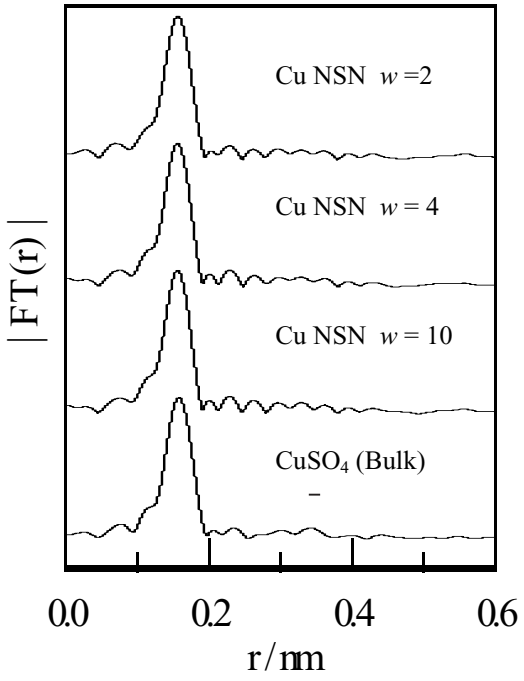

Figure 1 Fourier transforms of Cu K-edge EXAFS of Cu NSN and aqueous solution of $CuSO_4$.

Table 1. Structural parameters obtained by curve fitting.

w	CN	r_{Cu-O} / nm	σ^2 / 10^{-5} nm^2	ΔE_0 / eV
2	2.4	0.197	2.8	-3.7
4	2.5	0.197	3.0	-5.9
10	2.5	0.197	3.0	-6.0
Bulk	6*	0.197	7.1	-0.5

*: fixed parameter

References

[1] T. Ohkubo et al., J. Am. Chem. Soc. 124, 11860 (2002).
[2] T. Ohkubo et al., J. Phys. Chem. B 107, 13616 (2003).

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