

Hydration Structure around Cu²⁺ Restricted in Reverse Micelle of AOT

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Introduction

EXAFS technique is quite useful to obtain the hydration structure around a metal ion. Up to now, we applied EXAFS technique to study nano-scale ionic solution, which we named nanosolution (NSN) of RbBr, confined in the slit-shaped nanospaces of activated carbon fiber (ACF), showing hydration anomalies in the preceding papers [1-4]. 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 is described in this report as a function of concentration of dioctyl sulfosuccinate sodium salt (aerosol OT; AOT), which form reverse micelles in aqueous solution.

Experimental

We synthesized Cu(AOT)₂ sample from Cu(NO₃)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 CuSO₄) 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, which concentration is 50 mM, 100 mM, and 150 mM, respectively. Here, we fixed *w* values as 2 at which mean diameter of reverse micelles determined by the dynamic light scattering method were 3.5 nm. 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. These results show that a mean hydration number and distance between a Cu ion and an oxygen atom of water molecule for the NSNs 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 each other. 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 molecular assembly of AOT.

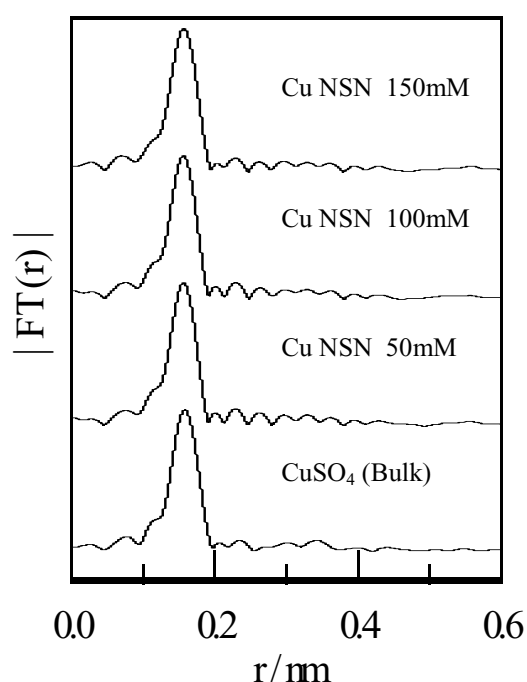


Figure 1 Fourier transforms of Cu K-edge EXAFS of Cu NSN and aqueous solution of CuSO₄.

Table 1. Structural parameters obtained by curve fitting.

<i>mM</i>	CN	<i>r</i> _{Cu-O} / nm	$\sigma^2 / 10^{-5} \text{ nm}^2$	$\Delta E_0 / \text{eV}$
50	2.6	0.197	2.8	-4.4
100	2.4	0.197	2.8	-5.8
150	2.3	0.197	2.8	-5.8
Bulk	6*	0.197	7.1	-0.5

*: Fixed parameter

References

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