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XAFS Structure Analysis of Hydrated Ions in Pores in Nanometer scale

Toshio YAMAGUCHI*, Koji YOSHIDA, Kaori INOUE, Ayaka TAKAKURA
Fukuoka Univ., Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

Introduction

The structure and properties of aqueous electrolyte solutions confined in pores in nanometer scale will differ from those in bulk due to both confinement and interfacial effects as in the case of confined water[1]. In the present study, the XAFS method has been applied to determine the structure of aqueous solutions of various I-I, II-I, and III-I electrolytes confined in MCM-41 of various pore sizes and ACF and to discuss the effect of pore size, ionic size, and temperature on the structure of ion hydration in the pores compared with those in bulk.

Experimental

Porous materials employed were MCM-41 C10 (pore diameter 21 Å), C14 (28 Å), and C18 (37 Å), provided by Prof. S. Kittaka (Okayama Univ. Sci.), and Activated Carbon Fiber (ACF), Maxsorb 20SPD (average diameter 20 Å) supplied by Kansai Thermo-chemical Ltd. Aqueous solutions of $Mn(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ga(NO_3)_3$, NaBr, $RbNO_3$ of concentration 0.5 M (= mol/dm^3), and of $AgNO_3$ of 1.5 M were prepared and introduced into pores. XAFS spectra were measured at the corresponding metal *K*-edges on BL-9C and AR-NW10A at the Photon Factory, KEK. The EXAFS spectra were analyzed with program ATHENA and ARTEMIS.

Results and Discussion

Figure 1 shows the Cu *K*-edge Fourier Transforms (not corrected for the phase shift) of 0.5 M $Cu(NO_3)_2$ aqueous solution confined in MCM-41 C10 and C14 and in bulk. The first peak at 1.4 Å is ascribed to the equatorial Cu-H_2O bonds in the aqua Cu^{2+} ions. The least-squares fitting analysis has showed that there are no substantial differences in structure of the aqua Cu^{2+} ion. A similar result was obtained for the other transition metal ions.

Figure 2 shows the Ag *K*-edge Fourier Transforms (not corrected for the phase shift) of a 1.5 M $AgNO_3$ aqueous solution confined in MCM-41 C18 as a function of temperature. The spectrum at 300 K shows the first peak at 1.65 Å, which corresponds to the Ag^+-H_2O bonds within the aqua Ag^+ ions. Interestingly, with decreasing temperature, the 1.5 Å peak gradually decreases and a new peak grows at around 2.7 Å. According to a previous work, the 2.7 Å peak was assigned to the Ag-Ag interactions within metallic silver[2]. This finding suggests that the silver ions are reduced to silver metal by X-ray irradiation in the pores. It should be noted that no such reactions take place in bulk at low temperatures. Thus, this reduction from the silver ion to silver metal is the one characteristic for confinement. Furthermore, reduction of silver ion to metallic silver has been confirmed by low temperature X-ray diffraction for the same system.

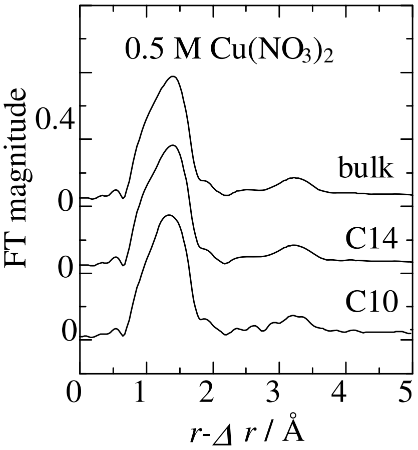

Fig.1. Cu *K*-edge Fourier Transforms for a 0.5 M $Cu(NO_3)_2$ aqueous solution confined in MCM-41 C14 and in bulk at 300 K.

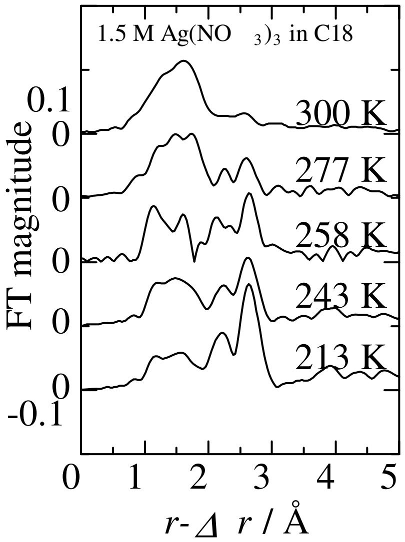

Fig.2. Ag *K*-edge Fourier Transforms of a 1.5 M $AgNO_3$ aqueous solution confined in MCM-41 C18 as a function of temperature.

References

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[2] T. Yamaguchi et al., Acta Chem. Scand. **A38**, 423 (1984).

*yamaguch@fukuoka-u.ac.jp