

The Structure of Ag^+ , Ca^{2+} and Y^{3+} Hydration in Confinement in Nanometer Scale over the temperature range of 298 – 190 K

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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 interaction with the pore wall as in the case of confined water [1]. With recent advances in nanotechnology, chemical processes in the nanoscale have become increasingly important where aqua ions play an important role in preparing nano materials, such as monometallic and bimetallic nanowires [2]. In this study, we have investigated the structure of ion hydration in 1.5 M AgNO_3 , and 1.0 M $\text{Y}(\text{NO}_3)_3$ aqueous solutions over the temperature range of 298 ~ 220 K and in an 1.0 M CaCl_2 aqueous solution at 298 K in confined geometry by X-ray absorption fine structure (XAFS) spectroscopy.

Experimental

Porous materials employed were mesoporous silica MCM-41 C10 (pore diameter 21 Å), C14 (28 Å), C18 (37 Å) and cross-linked polymer gel Sephadex G-15. Each aqueous solution was introduced into the corresponding porous materials with a VORTEX mixer. Inclusion of the sample solutions in the pores and their thermal behaviors in the temperature range 298~173 K were confirmed by differential scanning calorimetry (DSC). The Ag and Y *K*-edge XAFS spectra were measured over the temperature range of 298 – 190 K, whereas the Ca *K*-edge spectra were measured at 298 K at the Photon Factory, KEK. The corresponding solutions in bulk and Ag foil were also measured at 298 K as structural reference. The EXAFS spectra were analyzed with programs ATHENA and ARTEMIS. X-ray diffraction (XRD) measurements on the corresponding AgNO_3 sample were also made in the same temperature range by using an Mo *K* α radiation ($\lambda = 0.7107$ Å).

Results and Discussion

The DSC data have shown that the AgNO_3 aqueous solution remain in the liquid state in C10 and G15 in the measured temperature range, whereas three exothermic peaks due to ice formation appeared at 221, 233, and 251 K in C14. The Ag *K*-edge Fourier Transforms of the 1.5 M AgNO_3 aqueous solution confined in C10 have shown the presence of aqua Ag^+ as a predominant species throughout the temperature range measured. The Ag- H_2O distance were in the range of 2.34~2.38 Å as in bulk [3]. The hydration number of Ag^+ was found to ~4 at temperatures above 233 K and 4.5~5 below 223 K. This crossover in hydration number might be related to the structural transformation of high-density to low-density

water at ~223 K in C10 [4]. On the other hand, for the AgNO_3 solution in C14, the corresponding Fourier transform clearly showed that new Ag-Ag interactions are evolved, accompanied by a drastic decrease in the Ag^+ - H_2O peak with lowering temperature. The former was confirmed as due to formation of metallic silver by XRD and Ag *K* near-edge structure. Interestingly, such a reduction of Ag^+ to Ag in C14 did not take place by radiating Mo $K\alpha$ X-rays to the aqueous sample in C14 at low temperatures. For Ag^+ hydration in G-15, there appeared a predominant aqua Ag^+ together with a small amount of metallic Ag. In the case of Y^{3+} hydration, the Y *K*-edge data showed the aqua Y^{3+} are formed in all the pores over the temperature range. The Y^{3+} - H_2O distance and the hydration number were 2.38~2.40 Å and 7.5~8.2, respectively, independent of temperature, which is due probably to the strong electrostatic interactions between the trivalent Y^{3+} and water molecules. The Ca^{2+} *K*-edge data at 298 K have shown the presence of aqua Ca^{2+} are formed in all the pores. The Ca^{2+} - H_2O distance were 2.37~2.43 Å, and the hydration number of Ca^{2+} appeared to decrease from 7.2 in C10 to 5.6 in C18 and 4.8 in G15 with an increase in pore volume.

References

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