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A XAFS study on the anion exchange behavior of Cu-Cl Complexes in HCl solutions

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Introduction

There have been several investigations for the coordination environment of Cu^{2+} in copper chloride solutions [1]. The equilibrium constants indicate stepwise complexation from Cu^{2+} up to $CuCl_4^{2-}$ as possible species [2], and thus only their average coordination can be investigated by the previous studies. Our interest is to determine the structure of each Cu-Cl complex by XAS, and an anion exchange resin is introduced to extract anion species ($CuCl_3^-$ and $CuCl_4^{2-}$) and to remove the influence of the other complexes (from Cu^{2+} to $CuCl_2$).

Experimental

Three 0.1 M Cu aqueous solutions which contain 12, 7.0, and 3.0 M HCl were prepared. Cu-adsorbed resin samples were prepared from AG MP-1 (Cl- form, Bio-Rad Laboratories, Inc.) by the batch method equilibrated with the solutions above. The resins were then filtered, centrifuged, and sealed with polyethylene films for analysis. XAFS spectra at the Cu K-edge were taken in the fluorescence mode with Lytle detector using station BL-12C at KEK-PF. Cu K-edge spectra were calibrated with reference to the lowest energy inflection point in the spectrum of a copper metal foil fixed at 8980.3 eV. Data were analyzed using the REX2000 program (Rigaku Co.). All experimental procedures were performed at ambient temperature.

Results and Discussion

Presence of divalent copper was confirmed in the pre-edge region by a weak transition near 8976 eV (e.g. [3]) that is assigned to the 1s -> 3d transition (data not shown). EXAFS spectra of the solutions and resins in *k*-space are shown in Figs. 1(a) and 1(b) as $k^3\chi(k)$. In contrast to the solution spectra, which were variable depending on HCl concentrations (Fig. 1(a)), EXAFS spectra of adsorbed Cu chloro-complexes on the resins were identical despite different HCl concentrations used for equilibrium adsorption reaction (Fig. 1(b)). The uniform EXAFS spectra of Cu adsorbed on the resin despite the variation in Cu complexes in HCl solutions indicate a preferential adsorption of one species among anionic Cu chloro-complexes. The candidate of the adsorbed Cu anionic complex is $[CuCl_3]^-$ or $[CuCl_4]^{2-}$. A comparison of the distribution of the two complexes in HCl solution [4] with a few phenomena that a spectral similarity of the resin spectra to the Cu solution spectra in 12 HCl and a gradual increase of the amount of adsorbed Cu as the increase in Cl molarity indicates that the most plausible adsorbed complex is $[CuCl_4]^{2-}$. A comparison with Raman result was recently described [5].

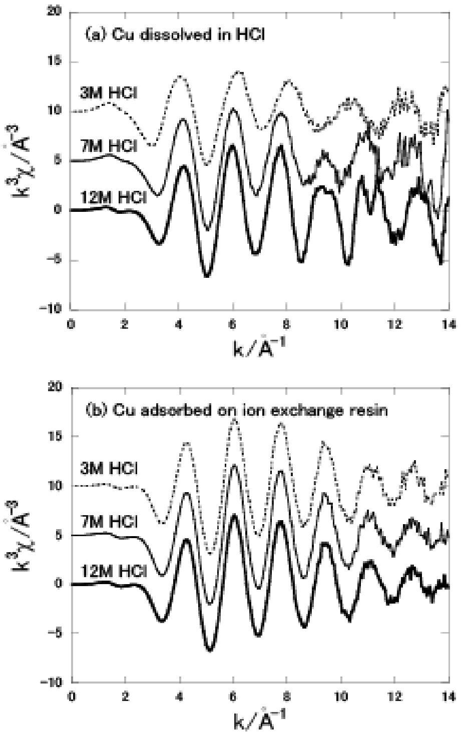

Fig. 1. Cu EXAFS k^3-weighted $\chi(k)$ plots for (a) Cu solution in 12 M, 7 M, and 3 M HCl and (b) Cu-adsorbed AG MP-1 anion exchange resin equilibrated in 12 M, 7 M, and 3 M HCl solutions.

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