Chemistry

Structural Study of Iron(III) Complexes with Bromide Ion in Solution

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Introduction

Stainless steels remain essentially passive, but they tend to corrode at specific areas and form deep pits in environments containing appreciable concentrations of Cl^- or Br^-. To elucidate the mechanism, it is important to understand the reactions between Fe, which is one of the main species in stainless steels, and water including anions. The complexation equilibrium and the structure of the component species are important to understand the reactivity of metal ions. In this study, the complexation reactions of Fe(III) with bromide ion have been investigated in aqueous and aqueous acetone solutions using XAFS technique.

Experiments

Sample solutions were prepared by dissolving iron(III) perchlorate hydrate and lithium bromide monohydrate into distilled water or aqueous acetone. The molar ratios of $[Br^-]/[Fe^{3+}]$ for samples were 0 ~ 13.5 for aqueous solution and 0 ~ 4.0 for aqueous acetone solution, respectively. XAFS spectra around the Fe K-edge were measured by the transmission mode at the NW2A beamline of PF-AR using an Si(111) double-crystal monochromator.

Results and Discussion

Radial structure functions of samples are shown in Figure 1, without the correction for the phase shift. The peaks around 150–160 pm in Fig. 1 (a) and (b) are assigned to the interactions between the Fe(III) ion and the oxygen atom of water molecules in the first hydration sphere: $Fe-O(H_2O^{1st})$. The interactions corresponding to the second hydration sphere are observed as broad peaks around 350 pm in Fig. 1 (a). With the increase in the molar ratio of $[Br^-]/[Fe^{3+}]$, new peaks appear around 210–220 pm in Fig. 1 (a) and (b), and peak intensities for $Fe-O(H_2O^{1st})$ are decreased. This tendency is more clear in aqueous acetone solution than in aqueous solution. These new peaks can be assigned to the Fe-Br interaction. The different results in two solutions indicate that the $[FeBr(H_2O)_5]^{2+}$ complex is formed in aqueous solution and that the higher order complexes with more bromide ions are also formed in aqueous acetone solution. This is considered to be mainly due to the lower dielectric property of acetone than water and the stronger solvation of bromide ion with water than acetone.

The Fe-O bond length of $[Fe(H_2O)_6]^{3+}$ in aqueous solution was obviously shorter than that in aqueous acetone solution, suggesting that the coordinating water
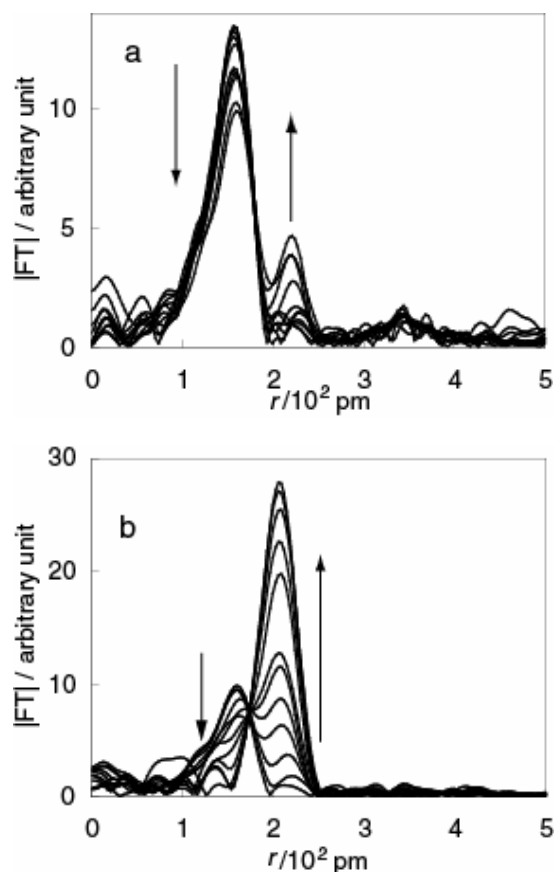

Figure1. Radial structure functions for various molar ratios of $[Br^-]/[Fe^{3+}]$ in aqueous solution (a) and in aqueous acetone solution (b).

molecules to the Fe(III) ion are polarized by the water molecules in the second hydration sphere due to the hydrogen bonding interactions. Furthermore, it is found that the peak around 150–160 pm is shifted to longer distance with the increase in the molar ratio of $[Br^-]/[Fe^{3+}]$ in aqueous solution. The Fe-O bond length (204 pm) in $[FeBr(H_2O)_5]^{2+}$ is found to be longer than that (201 pm) in $[Fe(H_2O)_6]^{3+}$ in aqueous solution according to the curve fitting analysis. The elongation is accounted by the electron donation from coordinating bromide ions to Fe(III) center, resulting in charge neutralization.

Authors have been investigating the corrosion mechanism with dispersive XAFS (DXAFS) instrument at NW2A. This study is expected to reveal dynamics of the corrosion mechanism.

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