

Determination of Structures of Cupric-Chloro Complexes in Hydrochloric Acid Solutions by X-ray Absorption Spectroscopy

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Introduction

High purity metals are indispensable for understanding the nature of materials in academic field. Anion-exchange separation is one of the most successful methods to remove metallic impurities, which yielded 99.999 mass% Fe, Co, Cu, and so on. However, the purity has been insufficient as source materials for semiconducting materials, such as β -FeSi₂ employed in advanced electronic devices. Thus, refining efficiency must be raised and anion-exchange separation has an unveiled ability. In order to raise the refining efficiency, the fundamentals of anion-exchange reaction must be clear. The thermodynamic analysis needs which metal-chloro complexes are adsorbed on anion-exchange resin and how they are distributed in the solution phase. The factor analysis followed by thermodynamic regression and FEFF fitting procedure was employed to UV-Vis and X-ray absorption spectra to determine the distribution and the structures of cupric-chloro complexes in hydrochloric acid solutions and copper is one of the most important substances as a base metal and an impurity in alloys.

Absorption spectrum, in general, is a summation of spectra of individual species in media and is represented by product of distribution, **C**, and spectra of each species, **E**, in a matrix form, $\mathbf{A} = \mathbf{C} \times \mathbf{E}$, where **A** is the matrix of the total absorption spectra. **A** can be decomposed into **C** and **E** mathematically, and **C** is unique whatever the absorption is. If an appropriate **C** is obtained from UV-Vis absorption spectra, XAS of individual species can be assessed by matrix division.

Experimental methods

Sample solutions contains a constant concentration of cupric species and varied concentrations of hydrochloric acid from 0 to 11 mol·dm⁻³. UV-Vis absorption spectra were measured using V-670 spectrometer (JASCO Corporation). The Cu K-edge XAS were collected using BL14B2 at Spring-8, Japan, with ring energy of 8 GeV.

Results and discussion

The thermodynamic properties of cumulative formation constants were derived by factor analysis followed by thermodynamic regression analysis. Consequently, there are five cupric species and their cumulative formation constants are, $\beta_1 = 0.165$, $\beta_2 = -0.197$, $\beta_3 = -2.38$, and $\beta_4 = -5.69$. Using the results, EXAFS spectra of the individual species were assessed according to matrix division of $\mathbf{E} = \mathbf{C} \setminus \mathbf{A}$, and theoretical model was fitted to them using Artemis and Feff 6L.02. As the results, the structures of cupric-chloro complexes were successfully determined as distorted octahedrons of $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_4^{\text{eq}}(\text{H}_2\text{O})_2^{\text{ax}}]^{2+}$, $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_4^{\text{eq}}(\text{H}_2\text{O})^{\text{ax}}\text{Cl}]^+$, and $[\text{Cu}^{\text{II}}\text{Cl}_2(\text{H}_2\text{O})_4^{\text{eq}}]^0$, a planar triangle of $[\text{Cu}^{\text{II}}\text{Cl}_3]^-$, and a tetrahedron of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$.

Conclusion

The decomposition of XAS of cupric-chloro complexes into individuals succeeded using the distribution by UV-Vis absorption spectra and their structures were determined for the first time. The obtained spectra can be referred as standards. Factor analysis is very useful and is expected to be employed in wide area.