

紫外可視/X線吸収分光成分分析および第一原理計算による 塩酸水溶液中銅(II)クロロ錯体分布と構造の決定

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Determination of Distribution and Structures of Cupric Chloro Complexes in Hydrochloric Acid Solutions using Factor Analysis of UV-Vis and X-ray Absorption Spectra and Validation using *ab-initio* Technique (¹*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○Masahito Uchikoshi,¹ Takatoshi Matsumoto¹

Attention should be paid to conditions of chemical species in aqueous solution employing ion-exchange and solvent extraction in the separation of metals besides extracting agents. Therefore, the distribution of cupric chloro complexes in hydrochloric acid solutions was investigated using factor analysis and validated using *ab-initio* technique.

An empirical estimation of a number of components was proposed. Distribution of cupric chloro complexes based on thermodynamic models was employed to decompose UV-Vis absorption spectra and the most possible thermodynamic model was optimized. The results were applied to X-ray absorption spectra (XAS) and those of the individual species were obtained. The structures of cupric chloro complexes were determined using FEFF fitting. Stable structures of cupric chloro complexes were calculated and compared with the structures determined experimentally. Consequently, the most reasonable distribution was determined; There were four cupric chloro complexes and their formation constants were successfully determined.

Keywords: Cupric chloro complex; Factor analysis; Distribution; *ab-initio* technique

イオン交換や溶媒抽出で金属を分離する際、官能基だけではなく、水相中のイオンの状態も重要である。本研究では、塩酸水溶液中の銅クロロ錯体の分布を成分分析法により調べ、第一原理計算による検証を実施した。

成分数の新しい推定方法を提案した。熱力学モデルによる錯体分布を用いて、紫外可視吸収スペクトルを分解し、最適化を行った。最適化された熱力学モデルを X 線吸収分光 (XAS) の分解に応用し、錯体個別の XAS を得た。FEFF によるフィッティングを実行し、銅クロロ錯体の構造を決定した。実験的に決めた構造と第一原理計算により求めた銅クロロ錯体の安定構造を比較検討し、最も確からしい熱力学モデルを決定した。その結果、4つの銅クロロ錯体が存在することが分かり、各々の安定度定数を決定した。

