Extraction Behavior of Copper(II) Cation Using Sulfonamide-type Polyanionic Chelators Having Ethylene Bridges

Chikako Kato and *Naoki Hirayama
Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University,
Kakuma-machi, Kanazawa 920-1192, Japan
Syunichi Oshima
Department of Chemistry and Biology Engineering, Fukui National College of Technology,
Geshi-cho, Sabae 916-8507, Japan

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Abstract
To research possible use of sulfonamide-type polyanionic chelators having ethylene bridges as extractants, extraction (cation-exchange) behavior of Cu\(^{2+}\) with several chelators was investigated. Tripod sulfonamide-type chelator, tris[2-(p-toluenesulfonamido)ethyl]amine, showed higher extractability than its monosulfonamide analog, 2-(p-toluenesulfonamido)ethylamine. Although the former can be generally considered as trianionic tetradentate chelator, on extraction of Cu\(^{2+}\), it acted as dianionic tridentate ligand and formed neutral 1:1 complex having one coordinating H\(_2\)O. The formed complex seems to be stabilized by chelate effect of the ligand and shielding effect of the coordinating sulfonamido group.

Key words: extraction, copper(II), sulfonamide, chelator

1 Introduction
Chelate extraction is a separation method for metals based on cation-exchange reaction between the metal cations and proton on an extractant. Therefore, the extractant should have at least one anionic donor atom, such as –O\(^{-}\) and –S\(^{-}\), formed by deprotonation. Sulfonamido groups (–NH–SO\(_2\)R) can deprotonate to produce stable anionic nitrogen donors (>N\(^{-}\)) and, therefore, possible use of many chelators having sulfonamido groups as extractants has been studied.[1-4] Recently, we reported that 2-(p-toluenesulfonamido)ethylamine (1, see Fig. 1), an N,N’- bidentate monoanionic ligand having simple ethylene bridge between the two donors, can extract Cu\(^{2+}\) at relatively high pH condition.[5] In this study, possible use of polyanionic chelators having p-toluene sulfonamid groups and ethylene bridge(s), such as 1,2-bis(p-toluene sulfonamido)ethane (2), N,N’,N”-tris(p-toluene sulfonyl)-diethylenetriamine (3) and tris[2-(p-toluene sulfonamido)-ethyl]amine (4), as extractant for Cu\(^{2+}\) was investigated, and evaluation concerning chelate effect in sulfonamide-type ligands for the enhancement of extractability was performed.

Fig. 1 Chemical structures of chelators 1-4.

2 Experimental
2.1 Reagents
Ligands 2-4 were synthesized by reacting excess of p-toluene sulfonfyl chloride with ethylenediamine, diethylenetriamine and tris(2-aminoethyl)amine, respectively, using similar manner to the synthesis of 1 [5]. Other chemicals were reagent-grade materials.
2.2 Extraction Procedure

In a centrifuge tube, 5 cm³ of chloroform containing 1×10⁻³ mol dm⁻³ of an extractant and 5 cm³ of aqueous phase containing 1×10⁻³ – 1×10⁻⁴ mol dm⁻³ of Cu²⁺, 1×10⁻¹ mol dm⁻³ of KNO₃ and 1×10⁻¹ mol dm⁻³ of buffer [acetic acid, 2-(N-morpholino)ethanesulfonic acid or 3-(N-morpholino)propane-1-sulfonic acid] were shaken at 25±1 °C for 1 h. After the two phases were separated, the pH and the metal concentration in the aqueous phase were determined using a pH meter and an atomic absorption spectrophotometer, respectively. The metal concentration in the CHCl₃ phase was determined after back-extraction into 1 mol dm⁻³ nitric acid.

3 Results and Discussion

The values of extraction percent (%E) of Cu²⁺ with the ligands 1-4 were plotted as a function of pH in Fig. 2. Dianionic chelators 2 and 3 showed no extractability for Cu²⁺. Probably, chelator 2 formed non-extractable dianionic 1:2 complex with Cu²⁺. In chelator 3, central N atom binds to p-toluenesulfonyl group and seems to show very low Lewis basicity, resulting in its no extractability. On the contrary, 4 showed higher extractability than monoanionic 1. The half-extraction pH values for 1 and 4 were obtained as 6.3 and 4.9, respectively.

Ligand 4 is considered generally as a trianionic tetradentate chelator, and can be abbreviated as H₃L. To determine the extracted Cu species in use of 4, slope analysis between logarithmic distribution ratio (log D) of Cu²⁺ and logarithmic initial concentration of 4 and that between log D and pH were performed. The results are shown in Fig. 3. The slope of the former was close to 1 and that of the latter was close to 2. Namely, the extracted species was determined as CuHL and the extraction equilibrium was determined as following cation-exchange one:

\[ \text{Cu}^{2+} + \text{H}_3\text{L}(o) \leftrightarrow \text{CuHL}(o) + 2\text{H}^+ \]

This result suggests that, on the extraction of Cu²⁺, 4 acts as N',N,N'-dianionic tridentate ligand and that one pendant arm in 4 is not contribute to the complexation. Since Cu²⁺ generally forms square planer complex, the CuHL complex seems to have one coordinating H₂O molecule. As reported previously [3], hydrated complexes of sulfonamide-type ligands often show high extractability because of shielding effect of the coordinating sulfonamido group near the H₂O. Furthermore, its higher extractability seems to be originated in the chelate effect. From this result, it is expected that sulfonamide-type polyanionic polydentate chelators having aliphatic bridges, which have flexible structure, can act as strong extractants for metal cations.

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References