

Development of Novel Calixarenes for Separation of Valuable Metals in Seawater by Computational Modeling

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S u m m a r y

Seawater contains various valuable metals such as uranium and lithium. Therefore, attempts are being made to develop highly selective extractants which recognizes target metal ions in reclaimed seawater. In this study, we have focused on the development of novel cyclic compound calixarene based extractants. A novel host compound calixarene, which is a cyclic compound connecting some phenol rings, is capable of forming several different extractant ring sizes and introducing various kinds of functional groups towards targeting of metal ion in seawater. Therefore, calixarene derivatives are capable of extracting valuable metals such as uranium, alkaline metals, heavy metals, rare earth metals and noble metals selectively by varying structural ring size and functional groups. The novel host compound calixarene has given promising results which lines it up as a potential extractant for the separation of valuable metal ions in seawater.

In the present study, the extraction behavior of alkaline, alkaline earth, and transition metals in liquid-liquid extraction was systematically investigated with a cyclic host compound calixarene carboxyl derivative. Using the novel host ligand, an extraction equilibrium experiment was carried out and the complexation mechanism between the metal ions and the cyclic ligand was investigated. Calixarene carboxyl derivatives showed high extractability for all of the metal ions compared to that of the monomer analog. The extraction behavior of alkaline and alkaline earth metals is closely related to the cavity size of the cyclic ligands; thus, the tetramer selectively extracted sodium and calcium ions, while the hexamer did so for cesium and barium ions. On the other hand, the extractability of transition metals could not be explained by a size effect, and increased in the order: monomer < tetramer < hexamer. Among transition metals, the higher the stability constant between a metal and the carboxyl group, the more preferential extraction was occurred. We also discussed the experimental results with a computational modeling by means of molecular mechanics and semi-empirical molecular orbital methods. The novel molecular mechanics (MM) calculation program MOMECC enables us to analyze stable conformation of a series of metal complexes.