

## Development and Computational Modeling of Novel Ligands for Selective Separation of Metal Ions in Seawater

Masahiro Goto and Kazuya Uezu  
Department of Chemical Systems & Engineering,  
Graduate School of Engineering  
Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

### 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 molecules that can recognize the target metal ion in the seawater. In the field of salt analysis, it is very important to develop an efficient ligand for a target salt ion, because the extractant has a crucial effect on separation and concentration of metal ions. In this study, we have focused on the novel cyclic ligand calixarene. The novel host ligand calixarene, which is a cyclic compound connecting phenol rings, is capable of forming different ring sizes and introducing various kinds of functional groups towards targeting of metal ions. Thus, 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.

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 carboxylic acid derivative. Using the novel host ligand, an extraction equilibrium experiment was conducted, and the complexation mechanism between the metal ions and the cyclic ligand was investigated. The extraction behavior is also discussed with computational modeling. The calixarene derivatives showed high extractability for all the salt ions compared to that of a noncyclic monomer analog. The extraction behavior of alkaline and alkaline earth metals is closely related to the cavity size of the cyclic ligands; the tetramer selectively extracted sodium and calcium ions, while the hexamer did so for cesium and barium ions. These results indicate that the cyclic structure is effective for recognizing alkaline and alkaline earth ions. All of the salt ions were confirmed to be extracted with the cyclic ligands by forming a 1 : 1 complex, which was also supported by the results of computational modeling. The novel molecular mechanics (MM) calculation program "MOMEC" enables us to analyze stable conformation of a series of metal complexes. These results show that cyclic ligands are useful and exhibit high selectivity when the cavity size fits the ionic size of a target ion.