4–3 Origin of Am/Cm Selectivity Elucidated by Chemical Bonding

—Focusing on the Covalent Interaction between Metal Ions and Separation Ligands—

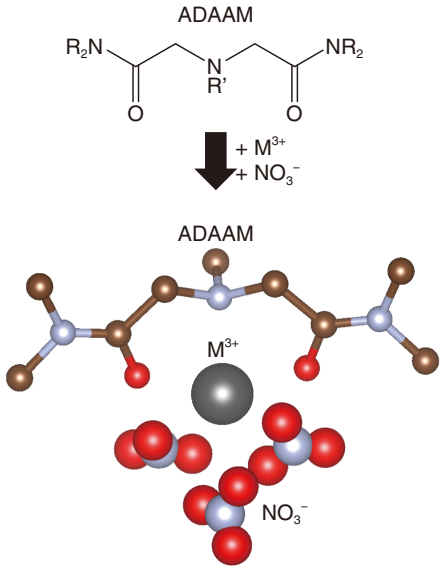

Fig.4-7 Structure of complex Am/Cm ion and an ADAAM separation ligand
Am and Cm ions (shown as metal ions) form a complex with one alkyldiamideamine (ADAAM) molecule and three nitrate ions. The lower picture shows the model complex including a metal ion, ADAAM, and nitrate ions.

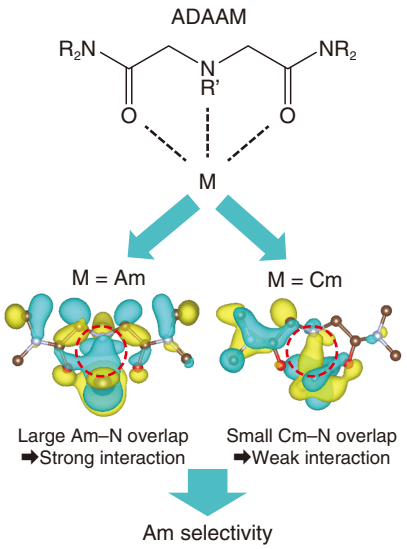

Fig.4-8 Interaction between Am/Cm ions and a molecular of ADAAM ligand
When analyzing the overlap of electron orbitals between the nitrogen atom of ADAAM and a metal ion (the red circle), the overlap between the Am ion and nitrogen atom is larger than that of the Cm ion and nitrogen atom, indicating a stronger interaction. This suggests that the difference in the interaction originates in the Am ion selectivity with ADAAM. The yellow and blue regions indicate the difference in the sign of phase in electrons as wave property.

To reduce the toxicity of high-level radioactive liquid waste (HLLW), the partitioning of minor actinides (MAs), which have extremely long half-lives, and the transmutation of short-life nuclides, partitioning and transmutation, has been developed. Although americium (Am) and curium (Cm) should be separated during partitioning due to the heat generating property of Cm, their similar chemical properties have made separation difficult. Therefore, We developed a process to selectively separate Am from Cm using alkyldiamideamine (ADAAM) as a separation ligand. Furthermore, the mechanism by which ADAAM shows higher selectivity of Am over Cm was clarified using a quantum chemical calculation.

Am and Cm exist as trivalent ions, Am^{3+} and Cm^{3+}, respectively, and form complexes with separation materials. The complex consisting of the metal ion (M^{3+}), nitrate ion (NO_3^-), and ADAAM was modeled as $[M(ADAAM)(NO_3)_3]$ (Fig.4-7), by referring to the result of the previous separation experiment (*1, *2). The Gibbs energy difference on the formation of each complex was then calculated to indicate that the Am complex is more stable than the Cm complex. The calculated value of the separation factor of Am from Cm was 6.2 and reproduced the experimental value, 5.5.

The coordination bonds between the metal ion and ADAAM were then examined with the aim of understanding the higher observed Am selectivity. ADAAM forms bonds with the metal ion using one amine nitrogen atom and two carbonyl oxygen atoms. Calculated result of coordination geometry revealed that the bond lengths between the metal ion and nitrogen atom of the ADAAM were 2.91 and 2.94 Å for the Am and Cm complexes, respectively. Furthermore, the covalent interactions of the coordination bonds were then analyzed by calculating the overlap of electron orbitals between the metal ion and nitrogen atom. The strength of the covalent interaction between atoms represents the degree of the overlap between electron orbitals. The overlap of the Am-N bond was larger than that of the Cm-N bond (Fig.4-8), thus indicating that the difference in the bonding strength between the metal ion and the ADAAM is a key to understand the Am/Cm selectivity. This work and future work on the selectivity in the separation of MAs is expected to contribute to the development of materials used for separating metal ions.

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*1 Sasaki, Y. et al., Extraction of Various Metal Ions from Nitric Acid to *n*-dodecane by Diglycolamide (DGA) Compounds, Journal of Nuclear Science and Technology, vol.44, no.3, 2007, p.405−409.

*2 Suzuki, H. et al., High-Performance Alkyl Diamide Amine and Water-soluble Diamide Ligand for Separating of Am (III) from Cm (III), Analytical Sciences, vol.33, issue 2, 2017, p.239−242.

Reference

Kaneko, M. et al., Theoretical Elucidation of Am(III)/Cm(III) Separation Mechanism with Diamide-Type Ligands Using Relativistic Density Functional Theory Calculation, Inorganic Chemistry, vol.57, issue 23, 2018, p.14513–14523.