

Selective Extraction of Cs(I) using Ionic Liquid Extraction System with Calix[4]arene-R14 and its application to separation for HLLW

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In order to separate the content of several long-lived radionuclides and significant fission product elements from high level liquid waste (HLLW), the extraction behavior of Cs(I) from nitric acid solution has been investigated using 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-Calix[4]arene (Calix[4]arene-R14) in combination with three types of ionic liquids, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_n\text{mim}][\text{NTf}_2]$ ($n=2,4,6$)). Calix[4]arene-R14 in the $[C_n\text{mim}][\text{NTf}_2]$ system can be used as a good choice for matching, and a high extraction efficiency can be achieved. These extraction systems exhibited high extraction efficiency and high selectivity for Cs(I) from simulated HLLW containing 25 typical elements and 2 M HNO_3 .

I. Introduction

To ensure a sustainable development of nuclear energy in the future, from the viewpoints of minimizing the long-term radiological risk and facilitating the management of HLLW for the reprocessing of the spent fuel, a partitioning of fission products (FPs) from HLLW is desirable. Especially, separation of Cs contributes to a reducing heat load and high radioactivity in HLLW because ^{137}Cs (half-life = 30.1 years) is one of the heat generating nuclide. For this purpose, to separate Cs(I) from the HLLW, we have been studying a novel partitioning process, which uses extractant in ionic liquid extraction system [1]. Ionic liquids (ILs) have attractive properties such as negligible vapor pressure, low flammability, thermal stability, etc. In this work, the selective extraction of Cs(I) from simulated HLLW (sHLLW) using 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-Calix[4]arene (Calix[4]arene-R14) as an extractant and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($[C_n\text{mim}][\text{NTf}_2]$) as solvents was studied, allowing comparison of the extraction behaviors with those using organic solvents. The investigation using the prepared Calix[4]arene-R14-loaded ionic liquid was carried out focusing on effect of acidity of aqueous phase, temperature, inorganic salts, and coexistent metal ions.

II. Experimental

Extraction behavior of Cs(I) from nitric acid solution has been investigated using extractant in combination with $[C_n\text{mim}][\text{NTf}_2]$ ($n = 2,4,6$). A macrocyclic supramolecular recognition agent, Calix[4]arene-R14 (98.7 %) was used without any further purification. The molecular structure of Calix[4]arene-R14 and $[C_n\text{mim}][\text{NTf}_2]$ are shown in Fig. 1.

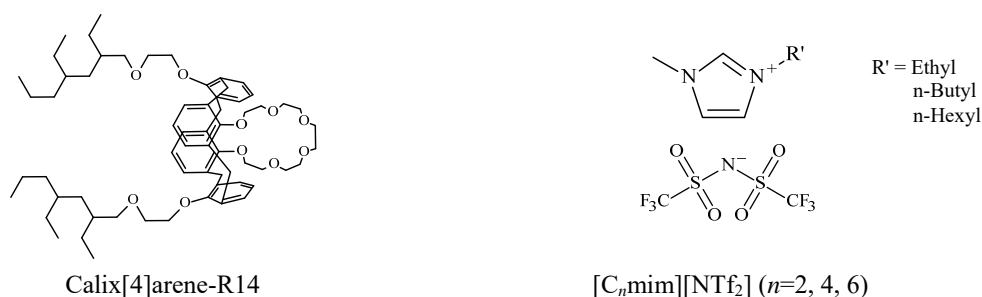


Fig. 1 Chemical structure of Calix[4]arene-R14 extractant, the cations $[C_n\text{mim}]^+$, and anions $[\text{NTf}_2]^-$.

Extraction experiments were conducted as follows: an aqueous solution (2 cm³) containing 5 mM (M = mol dm⁻³) Cs(I) ion was stirred with 2 cm³ of [C_nmim][NTf₂] containing Calix[4]arene-R14 in a thermostatic bath for 15 min, which was found to be sufficient for attaining equilibrium. After centrifugation, the upper aqueous phase was separated and the concentrations of Cs(I) and other metal ions were measured using an atomic absorption spectrophotometer (AAS) and inductively coupled plasma atomic emission spectrometer (ICP-AES). The concentration of the metal ions in the IL phase was calculated by subtraction of the determined amount in the aqueous phase from the total amount.

III. Results and Discussion

Effect of HNO₃ concentration on the extraction of Cs(I) is illustrated in Fig. 2. A decrease in the extraction efficiencies (E_{Cs}) for the three systems with increasing concentrations of HNO₃ is observed. These results suggest that one of the mechanisms for extraction is cation exchange. Several studies have reported that the extraction ratio decreases with an increase in the HNO₃ concentration [2]. The extraction results of Cs(I) by Calix[4]arene-R14 in dichloromethane and three [C_nmim][NTf₂] ILs under 2 M HNO₃ conditions are summarized in Table 1. All IL systems showed higher E_{Cs} value than dichloromethane system.

In addition, effect of other FP ions on the extraction of Cs(I) was investigated using sHLLW containing 25 elements and 2 M HNO₃ with the Calix[4]arene-R14/[C_nmim][NTf₂] at 298 K. All systems exhibited a high extraction efficiency and high selectivity for separation of Cs(I) from sHLLW. The separation factor of Cs from other elements such as Sr and platinum group metals showed large value. From the results, it was considered that Calix[4]arene-R14 in [C_nmim][NTf₂] systems could selectively and effectively extract Cs(I) from HLLW.

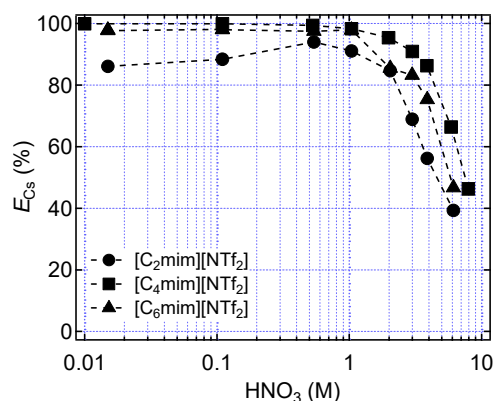


Fig.2. Dependence of E_{Cs} on HNO₃ concentration. [Calix[4]arene-R14] = 10 mM, [Cs] = 5 mM, T=298 K

Table 1 Results of extracting Cs(I) by Calix[a]arene-R14 in various solvents in 2 M HNO₃

solvent	E_{Cs} (%)
dichloromethane	78
[C ₂ mim][NTf ₂]	85
[C ₄ mim][NTf ₂]	95
[C ₆ mim][NTf ₂]	86

IV. CONCLUSIONS

The extraction behavior of Cs(I) from nitric acid solution has been investigated using Calix[4]arene-R14/[C_nmim][NTf₂] systems. The [C₄mim][NTf₂] systems can be used as a good choice for matching, and a high E_{Cs} can be achieved. These extraction systems exhibited high selectivity for Cs(I) from simulated HLLW. A novel partitioning process consisting of these systems for Cs(I) separation from HLLW was proposed and the experimental results indicated that the process is essentially feasible to separate the significant fission product elements from HLLW.

ACKNOWLEDGMENTS

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