

Complexation and Extraction of An(III) and Ln(III) with water-soluble SO₃-Ph-BTBP

Christoph Wagner^{a,b}, Udo Müllich^a, Andreas Geist^a, Petra J. Panak^{a,b}

^a*Institute of Nuclear Waste Disposal, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

^b*Ruprecht-Karls-Universität, Institut of Physical Chemistry, Heidelberg, Germany*

The recycling of minor actinides as nuclear fuel is complicated by the presence of curium due to its short term thermal power and neutron dose rate. Thus the development of processes for separating americium from curium are of particular interest. A new system was developed to separate only americium, addressing some of the challenges with the EXAm process such as a narrow pH window. The so called AmSel process uses water soluble SO₃-Ph-BTBP and TODGA's for Am(III), Cm(III), and Ln(III) separation. Am(III) + Cm(III) + Ln(III) distribution ratios as a function of HNO₃ and SO₃-Ph-BTBP concentrations were determined in extraction experiments. At low nitric acid concentrations the separation factor of Am(III) over Eu(III) exceeded 1000 and decreased with increasing acid concentration. The formation of 1:2 An(III)- and Ln(III)-aq-BTBP complexes was proven by time-resolved laser fluorescence spectroscopy (TRLFS) investigations of the aqueous phase after extraction. Furthermore, separation factors of Am(III) and Cm(III) for the aq-BTBP/TODGA system were determined at various experimental condition, varying between 1.5 and 3.2. The extraction studies revealed that stripping Am(III) from a loaded TODGA solvent is not impeded by slow kinetics. Buffers or salting out agents are not required.

For a better understanding of the selectivity of SO₃-Ph-BTBP towards An(III) over Ln(III) the complexation of Cm(III) and Eu(III) with SO₃-Ph-BTBP was studied by time-resolved laser fluorescence spectroscopy (TRLFS). Conditional complex formation constants of the 1:2 An(III) and Ln(III) complexes were determined at pH 3 and in 0.5 mol/L HNO₃. Though the stability constants of the 1:2 An(III) and Ln(III) complexes at 0.5 mol/L HNO₃ were lower by several orders of magnitude than at pH 3, the difference in the stability constants of two orders of magnitude between Cm(III) and Eu(III) remained constant. These results are in excellent agreement with the selectivity determined in the extraction studies and proves that the selectivity of SO₃-Ph-BTBP towards An(III) over Ln(III) is preserved even at highly acidic conditions. Furthermore, to explain the significant decrease of the stability constants of the 1:2 An(III) and Ln(III)-SO₃-Ph-BTBP complexes at 0.5 M HNO₃, fundamental studies on the impact of different parameters such as ionic strength, nitrate complexation and protonation of the ligand were performed. These studies revealed valuable mechanistic information on complexation reactions including the impact of competing reactions and/or ionic strength effects at various experimental conditions.