



Contribution ID: 145

Type: Verbal

Investigations of water-soluble salicylaldimine-based ligands for the separation of actinyl and non-actinyl cations

Tuesday, 13 May 2014 10:55 (14 minutes)

Current systems for the separation of actinide and lanthanide cations often employ organophosphorus reagents in combination or in sequence with anionic extractants under acidic conditions. Organophosphorous reagents do not often display large selectivity between trivalent actinides and lanthanides, as a consequence of the similar chemical properties of these elements and may require addition of soft donor ligands. Several of the actinides have higher oxidation states (e.g., V and VI) available under conditions in which they exist as linear dioxo cations. Under this configuration the actinides behave significantly different from trivalent lanthanides. The stability of these oxidation states can be a challenge for some transuranic actinides under acidic conditions. Studies suggest, however, that these oxidation states may be stabilized by coordination of ligands to the equatorial plane of the actinyl ion. For example, recent studies indicate that Schiff bases have been able to stabilize U(V). In light of these reports we are investigating ligands for the selective complexation of An(V/VI)-cations. Possible improvements in Ln/An separation factors may afford the design of separation systems under conditions not commonly considered for nuclear fuel and waste effluent processing.

In this paper we present results for the extraction of lanthanide(III) and actinyl(VI) cations from aqueous buffered solutions containing the water-soluble Schiff base N,N'-bis(5-sulfo-salicylidene)ethylenediamine (H₂SalenSO₃) by bis(2-ethylhexyl)phosphoric acid (HDEHP) in a suitable solvent. The effects of pH, buffer composition, and aqueous complex formation on the partitioning of metal ions are examined in terms of the ability of the aqueous ligand to retain actinyl ions while extracting non-actinyl ions. Spectroscopic and potentiometric titrations of H₂SalenSO₃ with UO₂²⁺ and NaOH have yielded valuable data, including conditional formation constants and ligand pK_a values. Both spectroscopic data and the crystal structure of the complex with UO₂²⁺ confirm that it has a 1:1 stoichiometry. Notably, visible spectroscopic measurements of solutions of the ligand with Nd(III) indicate that interactions between H₂SalenSO₃ and Ln(III) are quite weak. Combined with investigations of the effect of ligand hydrolysis on the formation of metal ion complex(es), the results indicate that optimum conditions for complexation occur at acidities lower than those typically maintained in f-element extraction by HDEHP. Therefore, competitive extraction studies have been carried-out at p[H] values between 5 and 6. Continuous contact experiments for U(VI) extraction by HDEHP in toluene in the presence and absence of H₂SalenSO₃ demonstrate that the uranyl ion distribution ratios (D) are less than 2 and holdback factors are substantial (D₀/D ≈ 100 to 800). Because both distribution ratios and holdback factors for Ln(III) extraction under similar conditions remain in the single digits, it is thought that the extent of aqueous ligand hydrolysis and the low acidity present challenges to maintaining extractable species. Investigations of the factors that lead to poor extraction of Ln(III) ions and the evaluation of similar, but more hydrolytically stable ligands, are ongoing.

Primary author: Dr HAWKINS, Cory (University of California, Irvine)

Co-authors: Mr BUSTILLOS, Christian (University of California, Irvine); Dr MAY, Iain (Los Alamos National Laboratory); Dr NILSSON, Mikael (University of California, Irvine); Dr COPPING, Roy (Los Alamos National Laboratory)

Presenter: Dr HAWKINS, Cory (University of California, Irvine)

Session Classification: Separation Methods, Speciation 2

Track Classification: Separation Methods, Speciation