Chemistry at the edge: actinide interactions with (poly)aminopolycarboxylates

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Research using (poly)aminopolycarboxylate (APC) ligands to achieve trivalent actinide / lanthanide separation has expanded significantly due to the development of derivative TALSPEAK solvent extraction processes that either simplify organic phase speciation (i.e. TALSQueak)[1] or streamline processing steps through combining neutral and organic phase extractants (i.e. TRUSPEAK or ALSEP)[2,3]. Courtesy their applications in over fifty years of actinide separation science, the best defined interactions of actinides with soft donors in aqueous solutions involve APC ligands. These interactions are usually defined in terms of stability constants, especially for the trans-americium actinides, with minimal dialogue regarding enthalpic and entropic contributions to the binding. While crystallographic, x-ray spectroscopic and computational techniques have provided support for covalency in actinide-ligand interactions[4]; examination of covalency trends for the trans-amercium actinides can become rapidly limited due to material availability, radiological hazards and experimental data to validate computational models. Consideration of APC thermodynamic data with heavier actinides could be instructive regarding fundamental f-element science. The benefit of producing lanthanide-normalized linear free energy diagrams, modeling previous actinide separations and review of actinide/N-donor complexation thermodynamics is considered. A first peek at data collected in the new on-campus radiochemistry facilities with trans-americium actinides is also provided.

[1] Braley, J.C.; Grimes, T.S.; Nash, K.L.; Alternatives to HDEHP and DTPA for Simplified TALSPEAK Separations. Ind. Eng. Chem. **2012**. *Ind. Eng. Chem. Res.,* 2012, 51(2) 629–638.

[2] Lumetta, G.J.; Gelis, A.V.; Braley, J.C.; Carter, J.C.; Pittman, J.W.; Warner, M.G.; Vandegrift, G.F.; The TRUSPEAK Concept: Combining CMPO and HDEHP for Separating Trivalent Lanthanides from the Transuranic Elements. *Solv. Ext. Ion. Exch.* **2013**, 31(3), 223-236.

[3] Braley, J.C.; Lumetta, G.L., Carter, J.C. Combining CMPO and HEH[EHP] for Separating Trivalent Lanthanides from the Transuranic Elements. *Solv. Ext. Ion. Exch.* **2013**, 31(6), 567-577.

[4] Polinski, M. J.; Garner, E., B.; Maurice, R.; Planas, N.; Stritzinger, J. T.; Parker, T. G.; Cross, J. N.; Green, T. D.; Alekseev, E. V.; Van Cleve, S. M.; Depmeier, W.; Gagliardi, L.; Shatruk, M.; Knappenberger, K. L.; Liu, G.; Skanthakumar, S.; Soderholm, L.; Dixon, D. A.; Albrecht-Schmitt, T. E., Unusual structure, bonding and properties in a californium borate. *Nature Chemistry* **2014,** *6* (3), 387-392.