

Project No. 10-881

Advanced Aqueous Separation Systems for Actinide Partitioning

Fuel Cycle

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In collaboration with:

Idaho National Laboratory

Pacific Northwest National Laboratory

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(Project 10-881) Advanced Aqueous Separation Systems for Actinide Partitioning
Final Report

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Project Scope:

One of the most challenging aspects of advanced processing of used nuclear fuel is the separation of transplutonium actinides from fission product lanthanides. This separation is essential if actinide transmutation options are to be pursued in advanced fuel cycles, as lanthanides compete with actinides for neutrons in both thermal and fast reactors, thus limiting efficiency. The separation is difficult because the chemistry of Am³⁺ and Cm³⁺ is nearly identical to that of the trivalent lanthanides (Ln³⁺). The prior literature teaches that two approaches offer the greatest probability of devising a successful group separation process based on aqueous processes: 1) the application of complexing agents containing ligand donor atoms that are softer than oxygen (N, S, Cl) or 2) changing the oxidation state of Am to the IV, V, or VI state to increase the essential differences between Am and lanthanide chemistry (an approach utilized in the PUREX process to selectively remove Pu⁴⁺ and UO₂²⁺ from fission products). The latter approach offers the additional benefit of enabling a separation of Am from Cm, as Cm(III) is resistant to oxidation and so can easily be made to follow the lanthanides.

The fundamental limitations of these approaches are that 1) the soft(er) donor atoms that interact more strongly with actinide cations than lanthanides form substantially weaker bonds than oxygen atoms, thus necessitating modification of extraction conditions for adequate phase transfer efficiency, 2) soft donor reagents have been seen to suffer slow phase transfer kinetics and hydro-/radiolytic stability limitations and 3) the upper oxidation states of Am are all

moderately strong oxidants, hence of only transient stability in media representative of conventional aqueous separations systems. There are examples in the literature of both approaches having been described. However, it is not clear at present that any extant process is sufficiently robust for application at the scale necessary for commercial fuel processing supporting transmutation of transplutonium elements. This research project continued basic themes investigated by this research group during the past decade.

In the Fuel Cycle Research and Development program at DOE, the current favorite process for accomplishing the separation of trivalent actinides from fission product lanthanides is the TALSPEAK process. TALSPEAK is a solvent extraction method (developed at Oak Ridge National Lab in the 1960s) based on the combination of a cation exchanging extractant (e.g., HDEHP), an actinide-selective aminopolycarboxylate complexing agent (e.g., DTPA), and a carboxylic acid buffer to control pH in the range of 3-4. Considerable effort has been expended in this research group during the past 8 years to elaborate the details of TALSPEAK in the interest of developing improved approaches to the operation of TALSPEAK-like systems. In this project we focused on defining aggregation phenomena in conventional TALSPEAK separations, on supporting the development of Advanced TALSPEAK processes, on profiling the aqueous complexation kinetics of lanthanides in TALSPEAK relevant aqueous media, on the design of new diglycolamide and N-donor extractants, and on characterizing cation-cation complexes of pentavalent actinides.

Project Objective:

Considered from the 30,000 foot view, the focus of this project was on developing new fundamental information to support advanced aqueous separations of minor actinides from fission product lanthanides. The four tasks pursued initially addressed:

1. the details of supramolecular organization in complex solvent extraction systems emphasizing TALSPEAK,
2. the impact of high temperature operations on SX performance,
3. the synthesis and characterization of soft donor extractants and structurally-hindered amides, and,
4. the stabilization of oxidized Am species through complexation with selected metal complexes.

After some investigation, the high temperature TALSPEAK studies proved to be intractable and to provide minimal improvement (possibly detriment) in TALSPEAK performance. To compensate, the soft donor portion of the program was expanded to include studies of DOTA complexes as separations reagents; this refocus also represents a continuation of the high temperature TALSPEAK studies, as these pseudo-TALSPEAK studies had to be done at elevated temperatures. The focus of Task 1 was broadened at the beginning of year 2 to incorporate a detailed investigation of the mechanism of lactate phase transfer catalysis in conventional TALSPEAK using fast reaction kinetics and a colorimetric indicator for lanthanide detection and to close-the-loop on the thermodynamics of conventional TALSPEAK; during the no-cost extension period concluded July 2014, the primary emphasis was on Advanced TALSPEAK kinetic studies in malonate media, new soft donor and diamide extractant synthesis, and characterization and continued emphasis on the characterization of pentavalent actinide cation-cation complexes.

From start to finish, this project has focused on developing new science to:

- Improve understanding of thermodynamics, kinetics and complex stoichiometry in TALSPEAK systems,
- Identify and/or synthesize new reagents (aqueous complexants, extractants and buffers) for TALSPEAK-like separations,

- Synthesize and characterize new derivatives of organic complexing agents suitable for application in trivalent actinide –lanthanide separations not necessarily based on TALSPEAK chemistry,
- Characterize actinide cation-cation interactions to assess their potential utility for isolation of oxidized Am species from PUREX raffinates,

And perhaps the most important objective, to:

- Educate a next generation of Ph.D. level actinide separation scientists.

Purpose:

This program focuses on developing improved understanding of TALSPEAK-like processes with the overarching objective of using the increased knowledge of fundamental interactions to develop improved options for application of this chemistry in advanced nuclear separations. Alternative approaches include studies of potential soft donor extractant molecules, structurally hindered extractants and of unique approaches to stabilizing Am(V) through the reaction of cation-cation complexes. Significant effort was expended in the synthesis and characterization of new reagents for separations applications, which is an under-represented component of the US fuel cycle research and development effort overall. These projects were designed to progress as independent but complementary activities defining individual Ph.D. research projects. As a measure of the impact of the educational mission of this project on DOE manpower needs, five Ph.D. dissertations and one chemistry Master's thesis were completed during this project with two dissertations and one master's thesis continuing with other means of support. Two of the Ph.D. graduates of this project are currently staff members at Department of Energy labs, two are in their second postdoctoral positions in nuclear research centers, and one former postdoc from this program is currently in a National Lab postdoc position. Three graduate students continue their studies, one working at the Pacific Northwest National Lab, another beginning a fellowship at the Idaho National Lab with financial supported derived from other sources.

Logical Path of the Research:

Parallel research thrusts assess different potential pathways to new approaches to actinide separations from fission product lanthanides. New compounds and new understanding of underlying principles foster increased understanding of options. One clear example of the value of the potential technological impact of fundamental chemical science studies is the ongoing development of the Advanced TALSPEAK process, which grew in part out of this research and our earlier investigations. Progress in amplifying knowledge leads to informed choices regarding new options for better separations opportunities. As new options become more attractive, focus shifts toward them and other concepts are reduced in importance, with the necessary constraint that advancing Ph.D. research demands a commitment to ultimately come to a conclusion. Educating the next generation of separation scientists cognizant of the challenges of nuclear fuel cycle separations is an overarching focus of the research activities of this group.

Outcomes:

This program started with the objective to develop as four parallel thrust areas: 1) knowledge of the drivers and details of supramolecular organization in TALSPEAK separations, 2) the impact of high temperature on TALSPEAK performance, 3) organic synthesis of new soft-donor complexants/extractants and structurally-hindered analogs of known phase transfer reagents, and 4) investigation of pentavalent actinide cation-cation complexes as a means of increasing redox stability of Am(V) for its selective isolation. The supramolecular characterization effort yielded fruit within the first year of the program and was re-characterized more broadly as Advanced TALSPEAK studies. This shift involved principally increased emphasis on an investigation of TALSPEAK complexation kinetics and ultimately on the introduction of alternate buffers into Advanced TALSPEAK systems. The elevated temperature study of TALSPEAK indicated

minimal improvement and possible reduced performance in conventional TALSPEAK at high temperature. This narrow thrust was abandoned at the beginning of year two with a shift of effort toward characterization of possible separations applications of the cyclic N-donor complexant DOTA as an “alternative” to DTPA in TALSPEAK-like separations. Since DOTA is a sterically demanding ligand exhibiting slow lanthanide complexation kinetics at ambient temperatures, most of this program was in fact conducted at elevated temperature. The ligand synthesis and cation-cation studies continued throughout. These projects were conducted as fundamentally independent activities designed to serve as the framework for graduate student Ph.D. thesis projects.

Five Ph.D. dissertations and one M.S. thesis were successfully defended based totally or in part on this work:

- Dr. Travis Shane Grimes, Ph.D. Dissertation, Inorganic Chemistry, May, 2011, *Coordination Chemistry of f-Elements in the TALSPEAK Process* (four open literature publications, two attributed in part to this project)
- Dr. John William Freiderich, Ph.D. Dissertation, Analytical Chemistry, August, 2012, *Pentavalent Actinyl Cation-cation Complexes in Aqueous and Non-aqueous Media* (Four open literature publications in advanced preparation stage)
- Dr. Courtney Leigh Hoch, Ph.D. Dissertation, Organic Chemistry, August, 2012, *Synthesis and Characterization of Novel Nitrogen-containing Ligands for Metal Ion Separations* (one publication in conference proceedings, additional publication based on continuation of the work by Dr. Muller)
- Dr. Jessica Ann Drader, Ph.D. Dissertation, Inorganic Chemistry, December, 2012, *Understanding and Utilizing DOTA Coordination Chemistry for Trivalent Lanthanide/Actinide Separations* (Two, possibly three open literature publications in advanced stage preparation)
- Dr. Derek McKenzie Brigham, Ph.D. Dissertation, Inorganic Chemistry, May, 2013, *Lanthanide Polyaminopolycarboxylate Complexation Kinetics in High Lactate Media: Investigating the Aqueous Phase of TALSPEAK* (Four open literature publications in preparation)
- Mr. Gabriel Johnson, M.S., Inorganic Chemistry, December, 2012, *Studies of the Thermodynamics of DTPA Complexation of the Rare Earth Elements at High Ionic Strength: Applications to the TALSPEAK Process* (One open literature publication in final revisions for publication)

Accomplishments:

- Extensive characterization of conventional TALSPEAK chemistry has been completed
 - Molecular-scale explanation of lactate buffer phase transfer kinetics enhancement in TALSPEAK developed
 - Advanced TALSPEAK separation based on combination of weaker (phosphonic acid) extractant and weaker aminopolycarboxylate complexant developed – lactate buffer acceptable, citrate buffer acceptable, malonate might enable lower pH operation and faster phase-transfer kinetics
 - Malonate buffer-DTPA trans-lanthanide complexation kinetics profiled
 - Malonate-based Advanced TALSPEAK separation was profiled

- Aggregation of Ln-Lactate-HDEHP explained by SANS study – mixed Ln-Lac-DEHP complexes only important at $[Ln]_{org} > 0.01M$
- New derivatives of polyaza complexants that exhibit useful affinity for trivalent actinides over lanthanides have been identified
 - When used with a co-extractant as phase transfer catalyst, a bipyridyl-bis triazole extractant exhibits rapid phase transfer kinetics, Am/Eu separation factors of 100, and easy stripping of extracted metals with simple pH shift.
- Potentially useful new insights into cation–cation complexes of pentavalent actinides open new opportunities for innovative approaches to americium-lanthanide separations
 - In polar non-aqueous solvents, Np(V)-Cr(III) complexes of significant stability are observed
 - Computational modeling supports observed strength of some actinyl cation-cation complexes.
- Several relevant publications in print or in press, many more in advanced stages of preparation
- Five new Ph.D. chemistry graduates and 1 M.S. chemistry student graduated with relevant experience. Four of these six remain active in actinide and separations research.
 - Two of these Ph.D. graduates are currently staff members at DOE labs.
 - Two participants in this research are currently Postdoctoral Research Associates at DOE labs
 - One Ph.D. graduate has recently begun a postdoctoral assignment at the CEA-Marcoule Atalante facility
- We have established significant enough potential in heterocyclic polyacetates (as represented by DOTA) to justify further examination of this class of ligands as effective reverse-TALSPEAK stripping agents with single-stage Am/Ln separation potential of 1000.
 - Structural features of lanthanide-DOTA complexes not previously recognized have been elucidated – a new mechanism is offered to explain slow lanthanide – DOTA complexation kinetics
 - A possible kinetics—based Ln/An separation based on DOTA has been demonstrated

Presentations

1. **Managing Transplutonium Actinides in Advanced Nuclear Fuel Cycles**, Ken L. Nash, Global 2011 Tenth International Conference, December 11-16, 2011, Makuhari Messe, Chiba, Japan
2. **Fundamental Studies of Aqueous Separations of f-Elements for Advanced Nuclear Fuel Cycles**, Kenneth L. Nash, Tokyo Institute of Technology 12/17/2011
3. **Fundamental Studies of Aqueous Separations of f-Elements for Advanced Nuclear Fuel Cycles**, Kenneth L. Nash. Nagoya University 12/9/2011
4. **Fundamental Studies of Aqueous Separations of f-Elements for Advanced Nuclear Fuel Cycles**, Kenneth L. Nash, Kitakyushu University 12/20/2011
5. **Thermochemistry of Solvent Extraction**. Kenneth L. Nash, Journee Scientifiques Marcoule, June 14-16, 2011, Marcoule, France
6. **Molecular-Scale Speciation Studies in Solvent Extraction: Lessons From TALSPEAK**, Nash, Kenneth L.; Grimes, Travis S.; Marie, Cecile; Uruga, Kazuyoshi; Johnson, Gabriel 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), I+EC-14.

7. **Separation Science in Advanced Nuclear Fuel Cycles** Nash, Kenneth L., 67th Northwest Regional Meeting of the American Chemical Society, Boise, ID, United States, June 24-27 (2012), NORM-43.
8. **Understanding the Chemistry of f-Elements Through Systematic Comparisons: A Pathway Toward Effective Fuel Reprocessing Strategies** K. L. Nash 245th American Chemical Society Meeting and Exposition, New Orleans, LA April 7-11, 2013 (invited)
9. **The Multiple Challenges of Americium Chemistry in Fuel Cycle Science and Technology** Kenneth L. Nash, *SACSESS 2013, Reading, UK, September 11-13, 2013* (invited)
10. **Heavy Element Separation Science: Challenges and Opportunities**, Kenneth L. Nash *Opportunities for Heavy Element Chemistry and Materials Workshop, Lawrence Berkeley National Lab, September 19, 2013* (invited)
11. **Molecular-Scale Speciation Studies in Solvent Extraction: Lessons From TALSPEAK** Kenneth L. Nash, Colorado School of Mines, Department of Chemistry, Golden CO, April 22-26, 2013 (invited)
12. **The TALSPEAK Process: Using Fundamental Chemistry to Unravel Complex Interactions** Kenneth L. Nash, Department of Energy Basic Energy Science Heavy Elements Chemistry/Separation Science Contractor meeting, April 22-25, 2013, (Invited Keynote Lecture)
13. **Actinide Separation Science to Define the Future of Nuclear Energy**, Ken Nash The University of Texas, Department of Chemistry, Austin ,TX, April 9, 2014 (invited)
14. **TALSPEAK-Like Separations at Elevated Temperatures Using 1,4,7,10-Tetraazacyclododecane-N,N',N'',N'''- Tetraacetic Acid: Complexation Kinetics** Drader, Jessica A.; Nash, Ken L. 66th Northwest Regional Meeting of the American Chemical Society, Portland, OR, United States, June 26-29 (2010), NORM-230
15. **Complexation Kinetics of Lanthanides and DTPA Under TALSPEAK-Like Aqueous Conditions** Brigham, Derek M.; Nash, Ken L. 66th Northwest Regional Meeting of the American Chemical Society, Portland, OR, United States, June 26-29 (2010), NORM-195.
16. **Small Angle Neutron Scattering (SANS) Studies to Determine the Aggregation State of the Organic Extractant Di-(2-ethyl(hexyl) Phosphoric Acid (HDEHP) in TALSPEAK** Travis S. Gimes, Kenneth L. Nash, Mark P. Jensen, Lisa Debeer-Schmidt, Ken Littell 35th Actinide Separations Conference, Charlotte, NC, May 23-26, 2011
17. **Explorations in Actinide Separation Science** (poster) K. L. Nash, C. Marie, T. S. Grimes, J. Freiderich, C. Hoch, J. Forster, C. Heathman, A. Johnson, J. Drader, M. Freiderich, D. Brigham, A. Shimada, J. Johnston, G. Johnson, T. Wall, 35th Actinide Separations Conference, Charlotte, NC, May 23-26, 2011
18. **Kinetic Study of DOTA as a Trivalent Ln/An Separations Agent for Advanced Fuel Reprocessing Schemes** (poster) J. A. Drader, K. L. Nash, 17th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 23-27, 2011
19. **Electrochemical Studies of Cation-Cation Complexes Involving UO₂⁺ and UO₂²⁺ in Chloride and Perchlorate Aqueous Systems** J. W. Freiderich, K. L. Nash, 17th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 23-27, 2011

20. **Solute Partitioning and Lanthanide Speciation in TALSPEAK Media** K. L. Nash, T. S. Grimes, C. Marie, 17th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 23-27, 2011
21. **Lanthanide Polyaminopolycarboxylate Complexation Kinetics in High Lactate Media: Investigating the Aqueous Phase of TALSPEAK Like Separations** Derek Brigham, Ken Nash, Actinide Separations Conference, Chattanooga, TN, May 21-24, 2012.
22. **Assessing the Potential of Lanthanide/Actinide Separations Based on the Tetraazamacrocyclic Ligand 1,4,7,10 Tetraazacyclododecane-N, N', N'', N'''-Tetraacetic Acid, DOTA.** Jessica A. Drader, Ken Nash, Actinide Separations Conference, Chattanooga, TN, May 21-24, 2012.
23. **Aqueous Chemistry of Cation-Cation Complexes Involving NpO_2^+ , UO_2^+ and UO_2^{2+} .** J. W. Freiderich, L. R. Martin, K. L., Nash Actinide Separations Conference, Chattanooga, TN, May 21-24, 2012.
24. **Calorimetric Determination of Lanthanide-DTPA Complexation Enthalpies at High Ionic Strength: Applications to the TALSPEAK Process** Johnson, Gabriel E.; Nash, Ken L., 67th Northwest Regional Meeting of the American Chemical Society, Boise, ID, United States, June 24-27 (2012), NORM-49.
25. **Fundamental Studies of AnO_2^+ Cation-Cation Complexes in Aqueous and Non-Aqueous Media** Freiderich, John W.; Martin, Leigh R.; Nash, Kenneth L., 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), NUCL-106.
26. **Ligand Design in Aqueous Separation Systems of Lanthanides and Actinides** Nash, Kenneth L., 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), NUCL-25.
27. **First Row Transition Metal Complexes with 2,6-Bis(1-Decyl-1h-1,2,3-Triazol-4-yl) Pyridine** Hoch, Cortney L.; Zeller, Matthias; Meier, G. P.; Nash, Kenneth L. 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), INOR-1271.
28. **Holdback Reagents in Solvent Extraction: Studies of Lanthanide Speciation in the TALSPEAK Process** Nash, Kenneth L.; Marie, Cecile; Grimes, Travis S.; Uruga, Kazuyoshi; Braley, Jenifer C., 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), IEC-50.
29. **Preliminary Trivalent Ln/An Separations Study with the Tetraazamacrocyclic Ligand 1,4,7,10-Tetraazacyclododecane-N,N',N'',N'''-Tetraacetic Acid, DOTA** Drader, Jessica A.; Nash, Kenneth L., 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), NUCL-76.
30. **Complexation Kinetics and Mechanism of Eu and DTPA Under TALSPEAK-Like Aqueous Conditions** Brigham, Derek M.; Nash, Kenneth L., 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), NUCL-61.
31. **Insights into f-Element Coordination Chemistry in TALSPEAK Systems** Kenneth L. Nash, Gabriel Johnson, Cecile Marie, Travis S. Grimes, Jenifer C. Braley, Atalante 2012, Nuclear Chemistry for Sustainable Fuel Cycles, Sept. 2-7, 2012, Montpellier, France

32. **Nitrogen Donor Systems for An(III)-Ln(III) Separations** Kenneth L. Nash, Jessica Drader, Colt Heathman, Cortney Hoch, Derek Brigham, Mark D. Ogden, Jenifer C. Braley, Mikael Nilsson, Atalante 2012, Nuclear Chemistry for Sustainable Fuel Cycles, Sept. 2-7, 2012, Montpellier, France
33. **Building on the Past, Considering New Options and Reagents: Minor Actinide Separation Research at WSU** Kenneth L. Nash, Colt Heathman, Aaron Johnson, Derek Brigham, 37th Annual Actinide Separations Conference, Spokane, WA, June 24-27, 2013
34. **Teasing Out the Details of TALSPEAK Separations Using Multiple Modes of Analysis** K. L. Nash, T. S. Grimes, C. Marie, D. Brigham, G. Johnson, K. Uruga, M. Nilsson 245th American Chemical Society Meeting and Exposition, New Orleans, LA April 7-11, 2013
35. **Advancing the Scientific Basis of Trivalent Actinide-Lanthanide Separations** Kenneth L. Nash, Global 2013, Nuclear Energy at a Crossroads, September 29-October 3, 2013, Salt Lake City, Utah
36. **Minor Actinide Separation Research at WSU: New Insights, New Systems, New Reagents** Kenneth L. Nash, Colt R. Heathman, Aaron T. Johnson (and others), DOE – NE Fuel Cycle R&D Working Group meeting, Albuquerque, NM, April 2-4, 2013
37. **Synthesis and Characterization of A New N-Containing Ligand for An/Ln Separation** Julie M. Muller, Kenneth L. Nash, 247th National ACS Meeting, March 16-20, 2014, Dallas, TX
38. **Patterns of Stability in f-element separations: trans-lanthanide trends in solvent extraction** K. L. Nash, 248th National ACS meeting, August 10-14, 2014, San Francisco, CA I&EC 18
39. **Novel addition of 1,2,3-triazole rings on a bipyridine-based ligand for actinide(III)-lanthanide(III) separations** J. M. Muller, K. L. Nash, 248th National ACS meeting, August 10-14, 2014, San Francisco, CA I&EC 22

Publications

1. **The Role of Carboxylic Acids in TALSQUEAK Separations** Braley, J.C., Carter, J.C., Sinkov, S.I., Nash, K.L., Lumetta, G.J. *J. Coordination Chemistry* (2012) 65(16), 2862-2876.
2. **Small Angle Neutron Scattering (SANS) Study of Organic Phase Aggregation in the TALSPEAK Process**, Travis S. Grimes, Mark P. Jensen, Lisa Debeer-Schmidt, Ken Littrell, Kenneth L. Nash *J. Phys. Chem. B.* (October 2012) x.doi.org/10.1021/jp306451d | *Journal of Physical Chemistry B* (2012), 116(46), 13722-13730.
3. **Kinetics of Lanthanide Complexation by EDTA and DTPA in Lactate Media** K. L. Nash, D. Brigham, T. C. Shehee, A. Martin, *Dalton Transactions* (2012), 41(48), 14547-14556.
4. **The Chemistry of TALSPEAK: A Review of the Science** Kenneth. L. Nash *Solvent Extraction & Ion Exchange* (2015) 33(1) 1-57. DOI 10.1080/07366299.2014.985912
5. **Advanced TALSPEAK Separations Using a Malonate Buffer System** Joseph L. Lapka and Kenneth L. Nash *Solvent Extraction and Ion Exchange* (2015) 33, pp DOI 10.1080/07366299.2015.1012878

6. **Complex Interactions in Solvent Extraction—Biphasic Speciation in the TALSPEAK Process** Kenneth L. Nash, Mikael Nilsson, Travis Grimes, Jenifer Braley, Kazuyoshi Uruga and Cecile Marie, 19th International Solvent Extraction Conference Proceedings, October 3-7, 2011, Santiago, Chile, Ch 3, paper 85.
7. **Insights into f-Element Coordination Chemistry in TALSPEAK Systems** Kenneth L. Nash, Gabriel Johnson, Derek Brigham, Cecile Marie, Travis S. Grimes, Jenifer C. Braley Proceedings ATALANTE 2012 – Nuclear Chemistry for Sustainable Fuel Cycles *Procedia Chemistry* Volume 7, 2012, Pages 45–50, ATALANTE 2012 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles <http://dx.doi.org/10.1016/j.proche.2012.10.009>
8. **Advancing the Scientific Basis of Trivalent Actinide-Lanthanide Separations** Kenneth L. Nash Proceedings Global 2103, Nuclear Energy at a Crossroads, September 29-October 3, 2013, Salt Lake City, Utah, pp. 899-906
9. **Synthesis and characterization of a new N-donor ligand for An(III)/Ln(III) separation** Julie M. Muller, Kenneth L. Nash Proceedings International Solvent Extraction Conference 2014, Wurzburg, Germany, September 7-11, 2014 paper number 8948

In Progress publications:

10. **Improved understanding of the Ln(III)-DOTA complex formation mechanism,** Jessica A. Drader, Kenneth L. Nash in preparation for publication in *Inorganic Chemistry*
11. **Kinetics of the complexation of lanthanides by DTPA in malonate media** G. Ferru and K. L. Nash in preparation for publication in *Dalton Transactions*
12. **Thermodynamics of [NpO₂·M]⁴⁺ Complexes Involving Cr³⁺ and Lu³⁺ in Mixed-Solvent Media** John W. Freiderich, Leigh R. Martin, Kenneth L. Nash in preparation for publication in *Inorganic Chemistry*
13. **Thermodynamics of Actinyl Cation-Cation Complexes in Aqueous Media, Part I: [UO₂·UO₂]³⁺ Complexes** John W. Freiderich, Leigh R. Martin, Kenneth L. Nash in preparation for publication in *Inorganic Chemistry*
14. **Thermodynamics of Actinyl Cation-Cation Complexes in Aqueous Media, Part II: [NpO₂·UO₂]³⁺ Complexes** John W. Freiderich¹, Leigh R. Martin², Kenneth L. Nash³ in preparation for publication in *Inorganic Chemistry*
15. **Studies of the Thermodynamics of DTPA Complexation of the Rare Earth Elements at High Ionic Strength: Applications to the TALSPEAK Process** Travis S. Grimes, Gabriel E. Johnson, and Kenneth L. Nash in preparation for publication in *J. Solution Chemistry*
16. **Synthesis of a new nitrogen-containing ligand for actinide/lanthanide separations and characterization of its Ln(III) complexes** Julie M. Muller, Kenneth L. Nash in Preparation for publication in *Inorganic Chemistry*
17. **Exploration of the complexation of selected lanthanide ions by aminopolycarboxylic acids in concentrated lactate buffer media,** Derek M. Brigham, Kenneth L. Nash, in preparation for publication in *Inorganic Chemistry*
18. **Back extraction of Am³⁺, Eu³⁺, and Nd³⁺ under separations conditions: A kinetic investigation and examination of M(H₂DOTA)⁺ and M(DOTA)⁻ kinetic behavior in**

solvent extraction. Jessica Drader, Kenneth L. Nash. In preparation for publication in Solvent Extraction and Ion Exchange

Project organizational details:

The project organization was such that weekly research group meetings were held with all members of this research team and the remaining members of the research group (funded in other projects) present. In addition, our research team interactions are such that frequent ad hoc one-on-one meetings are held, almost on a daily basis. The aqueous separation focus of all of this work in general provides complementary information, thus it is expected that the parallel observations will support the creation of more useful knowledge that could ultimately lead to new used fuel processing options. The cross cutting weekly group meetings regularly inspire the cross fertilization of ideas between the several different projects active in the research group. For example, work funded by the FCR&D Sigma Team for Minor Actinide Separations program has benefitted from the insights developed in the TALSPEAK kinetics investigation. During the no-cost-extension portion of this program, the soft-donor and structurally- hindered extractant projects, TALSPEAK reaction kinetics, and the investigation of cation-cation complexes were continued; during this extension period, the DOTA project was suspended.

The payoff of this approach is in the development of more robust separation systems that perform predictably. As with all graduate education activities, an equally important outcome is the human capital of trained scientists with specific knowledge relevant to sustained innovation in nuclear fuel cycle research and development. Much of the research conducted in this program focuses on TALSPEAK-like applications in which trivalent actinides are selectively retained in the aqueous phase while lanthanides are extracted. Where appropriate, we also examine the chemistry of uranium, neptunium, and plutonium for their intrinsic interest, their relevance to advanced fuel cycle development, and to give young investigators an opportunity to work hands-on with these actinides, arguably the most interesting elements in the periodic table.

Students and postdocs are encouraged to act independently in this program, but to seek advice as needed from the PI, National Lab partners, and colleagues. As is true of all research, productivity always increases geometrically (sometimes exponentially) with knowledge. With young investigators their limited experience often results in comparatively low productivity that inevitably (for successful Ph.D. students) increases with the mistakes made along the way. It is how we best learn new skills.

Results: As a final report on the project, the focus in this document is on experimental work conducted during the period August 1, 2010 and the extended conclusion date of June 30, 2014. Interpretation and correlation of these results is continuing in some areas as time is available. These activities include outcomes of:

- 1) Complexation kinetics, thermodynamics, solvent aggregation in conventional TALSPEAK and some Advanced TALSPEAK process development,
- 2) Profiling of the complexing kinetics and separations potential of DOTA,
- 3) Synthesis and characterization of new N-donor extractant molecules,
- 4) Characterization of pentavalent actinide cation-cation complexes.

The supramolecular organization aspects of the study and high temperature TALSPEAK were completed during the first 1.5 years of this program. The structurally hindered extractant program suffered an unexpected setback when the graduate student responsible for the research developed some significant legal problems and was forced to leave graduate school. Another student (Ph.D. candidate Ben Tokheim) assumed responsibility for this project and has done some scaled back studies of this subject during the extension period; the experimental results on

this task have been approached as a scoping exercise, are preliminary, and will not be discussed in detail here. The preliminary results proved encouraging and we plan eventually to seek additional funding to continue the work. For reporting purposes, the focus of the following narrative will be on the four numbered tasks above. Each of these four projects produced one new Ph.D. chemistry graduate during FY 2013. The soft donor extractant project continued in the competent hands of postdoctoral associate Dr. Julie Muller. The continuation of the cation-cation studies has focused on non-aqueous media and was conducted by Ph.D. candidate Adam Burn.

Task 1. TALSPEAK thermodynamics, supramolecular organization of solutes, and phase transfer kinetics. Investigations of the fundamental chemistry of the TALSPEAK process have produced several lines of evidence that strongly suggest that a fundamental change in the extraction behavior of the organic phase occurs as the lactate concentration increases. Water content and lactic acid partitioning into the organic phase abruptly increase at lactate concentrations above 0.5 M; lactate (primarily lactic acid – HLac) partitioning into the extractant phase also increases as pH rises (of course, the ratio of HLac/NaLac actually decreases as pH rises). This result has been interpreted to indicate an unexpected salting out effect deriving from the relatively complex structure of the lactate anion. The results of other experiments support the premise that NaLac has a profound effect on water activity in these highly non-ideal solutions. Solute-solvent interactions in this system, which operates at far from ideality in both the aqueous and organic phases, are very complex. Phase transfer kinetics are slower than the respective homogeneous phase kinetics would predict. The following attempts to provide some additional clarity on the basic chemistry of conventional TALSPEAK.

Subtask 1a. Thermodynamics of ligand protonation and complexation reactions in TALSPEAK systems

Thermodynamic modeling of conventional TALSPEAK was a hallmark of our earlier investigations of TALSPEAK chemistry. One final limitation to the accuracy of the thermodynamic modeling of TALSPEAK was the reliance on Ln-DTPA stability constant and ligand protonation constants from the prior literature. In the calculations done previously, it proved impossible to find in the existing literature a completely consistent set of thermodynamic equilibrium constants describing all possible reactions. The most important matching of conditions was made between ligand protonation and complexation constants for lactate and DTPA. Literature data for extraction equilibria are far less consistent (and suffer the effects of a wider array of variables). Of particular concern was the need to match $I = 2.0$ M lactate data with $I = 0.1$ M DTPA data. To reduce the uncertainty of the modeling from this factor, fresh estimates were made of the thermodynamic parameters describing lanthanide-DTPA interactions at 2 M ionic strength (NaClO_4) and 25.0°C.

Protonation equilibrium constant data reported by Grimes are report in Table 1. Lanthanide complexation equilibrium constant values are given in Table 2. DTPA protonation constants are defined for the successive protonation equilibria. Lanthanide-DTPA complexation equilibrium constants are defined as $b_{mhl} = [M_m H_h L_l] / [M^{3+}]^m [L^{5-}]^l [H^+]^h$. Based on a comparison with the prior literature, the protonation constants most affected by ionic strength are the first and second equilibria. From examination of the 0.1 M and 2.0 M ionic strength data from the literature, it is apparent that, while selected equilibrium constants are larger at 0.1 M than at 2.0 M, the relative magnitude of protonation and metal complex stability vary consistently, thus internally-consistent data sets might be expected to produce a reasonable representation of equilibrium speciation in TALSPEAK systems. Care must be taken in assembling data sets for such modeling to match as closely as possible the conditions for parameter sets to maximize accuracy of predictions.

Species	log K _a ^a	log K _a ^b
HL	9.50 ± 0.01	9.20 ± 0.01
H ₂ L	8.31 ± 0.01	8.06 ± 0.01
H ₃ L	4.38 ± 0.01	4.25 ± 0.01
H ₄ L	2.53 ± 0.03	2.68 ± 0.01
H ₅ L	2.41 ± 0.01	2.03 ± 0.03
H ₆ L		1.96 ± 0.02

Table 1. Acid dissociation constants in 2.0 M NaClO₄ and sodium triflate.

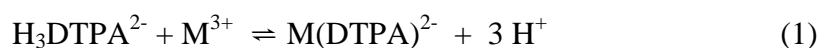
^aNaClO₄ used as background electrolyte.

^bSodium triflate used as background electrolyte.

Metal	log β ₁₀₁	log β ₁₁₁	log K ₁₁₁
Y	20.13 ± 0.02	21.87 ± 0.04	1.74 ± 0.03
La	18.02 ± 0.02	20.38 ± 0.03	2.36 ± 0.03
Ce	19.06 ± 0.01	20.77 ± 0.02	1.72 ± 0.02
Pr	19.64 ± 0.01	21.34 ± 0.02	1.71 ± 0.02
Nd	20.23 ± 0.01	21.57 ± 0.05	1.34 ± 0.04
Sm	20.79 ± 0.01	22.39 ± 0.02	1.59 ± 0.02
Eu	21.03 ± 0.01	22.56 ± 0.03	1.54 ± 0.02
Gd	21.15 ± 0.02	22.38 ± 0.02	1.23 ± 0.02
Tb	21.15 ± 0.01	22.77 ± 0.02	1.61 ± 0.02
Dy	21.23 ± 0.01	22.81 ± 0.02	1.58 ± 0.02
Ho	21.43 ± 0.02	22.76 ± 0.05	1.33 ± 0.05
Er	21.41 ± 0.02	22.66 ± 0.05	1.25 ± 0.05
Tm	21.10 ± 0.02	22.45 ± 0.05	1.35 ± 0.04
Yb	20.96 ± 0.01	22.53 ± 0.02	1.57 ± 0.02
Lu	21.14 ± 0.01	22.21 ± 0.05	1.07 ± 0.05
	2.0 M NaTriflate		
Eu	20.74 ± 0.01	22.48 ± 0.02	1.74 ± 0.02

Table 2. Free energy and stability constants for Ln·DTPA²⁻ complexes in NaClO₄ and sodium triflate at 25 °C.

It can be seen in an examination of these data that equilibrium constants are 50-100 times lower at 2.0 M ionic strength than at 0.1 M (as is typically seen). However, ligand protonation equilibrium constants are also lower at 2.0 M ionic strength (though the first and second ligand protonation reactions are more significantly impacted). Considering that the dominant DTPA free ligand species at pH 3.6 is H₃DTPA²⁻, the effective metal complexation reaction in TALSPEAK aqueous phases is:



for which a few representative equilibrium constant values ($\log \beta_1 - \log (K_{h1} \cdot K_{h2} \cdot K_{h3})$) are: $\text{La}^{3+} = -3.88$ ($I = 0.1 \text{ M}$), -4.27 ($I = 2.0 \text{ M}$), $\text{Nd}^{3+} = -1.76$ ($I = 0.1 \text{ M}$), -1.96 ($I = 2.0 \text{ M}$), $\text{Eu}^{3+} = -0.97$ ($I = 0.1 \text{ M}$), -1.16 ($I = 2.0 \text{ M}$), $\text{Tb}^{3+} = -0.65$ ($I = 0.1 \text{ M}$), -1.04 ($I = 2.0 \text{ M}$). It can be seen that, although the metal complex “stability constants” may differ significantly, the compensating change in affinity for H^+ tends to offset the impact of this change. A more important impact would be seen in comparing the relative strength of competing complexants (e.g., lactate vs. DTPA) if the equilibrium constants were not determined at the same ionic strength and temperature.

It is also necessary in some cases to consider the internal consistency of tabulated thermodynamic parameters. Among the compiled data describing lanthanide lactate complexes at 2.0 M ionic strength, as shown in Figure 1, most of the reported data is internally consistent. However, selected values in the compilation are not consistent with the other 80% of the data (they have been eliminated from this plot). For purposes of the modeling to be shown below, polynomial functions were developed (Origin 7.5) and the suspect data were “improved” with estimates based on interpolation (a reasonable approach to refining thermodynamic data trends probably most reliably employed only within the lanthanide series) shown in Table 3. Using this internally-consistent data set, speciation plots were constructed.

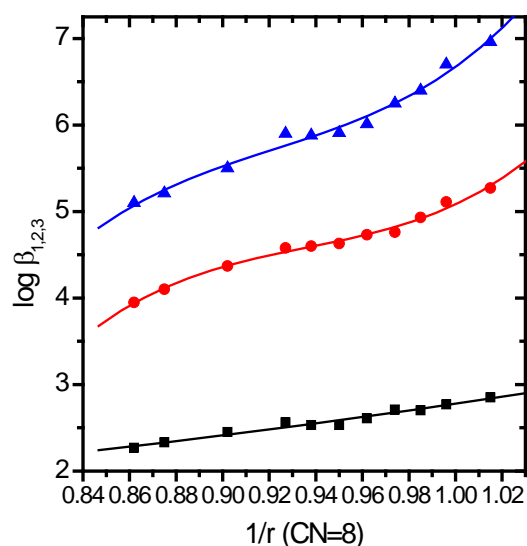


Figure 1. Correlation of experimental data on lanthanide-lactate complexes from the NIST Critical Stability Constants database and estimates of missing/inconsistent data describing lanthanide lactate stability constants $I = 2.0 \text{ M}$, $T = 25.0^\circ\text{C}$ (\blacktriangle) $\log \beta_1$, (\bullet) $\log \beta_2$, (\blacksquare) $\log \beta_3$. Lines represent polynomial ($n = 4$) fit of the data (to enable interpolation of improved values for less certain constants).

Lanthanide Lactate complex stability						Extraction Equilibria		
Ln	1/r cn8	log β_1	log β_2	log β_3	ΔG_{MLac3}	log K_{ex}	ΔG_{ex}	ΔG_{LnDTPA}
La	0.86199	2.27	3.95	5.1	-29.1	-2.22	+12.7	-102.8
Ce	0.87497	2.33	4.1	5.21	-29.7	-1.77	+10.1	-108.8
Pr	0.88802	(2.36)	(4.26)	(5.40)	-30.8	-1.46	+8.3	-112.1
Nd	0.90204	2.45	4.37	5.5	-31.4	-1.32	+7.5	-115.5
Pm	0.915	(2.45)	(4.49)	(5.67)	-32.4	-0.98	+5.6	-----
Sm	0.92704	2.56	4.58	5.9	-33.7	-0.50	+2.8	-118.7
Eu	0.938	2.53	4.6	5.88	-33.6	-0.22	+1.3	-120.0
Gd	0.95003	2.53	4.63	5.91	-33.7	-0.06	+0.3	-120.7
Tb	0.962	2.61	4.73	6.01	-34.3	+0.63	-3.6	-120.7
Dy	0.97399	2.71	4.76	6.25	-35.7	+0.95	-5.4	-121.2
Ho	0.98503	2.7	4.93	6.4	-36.5	+1.24	-7.1	-122.3
Er	0.99602	2.77	5.11	6.7	-38.2	+1.59	-9.1	-122.2
Tm	1.00604	(2.79)	(5.17)	(6.84)	-39.4	+1.99	-11.3	-120.4
Yb	1.01502	2.85	5.27	6.96	-39.7	+2.48	-14.2	-119.6
Lu	1.02396	(2.89)	(5.47)	(7.25)	-41.4	+2.75	-15.7	-120.6

Table 3. Recommended log β_{lac} and K_{ex} values (HDEHP extraction) for conventional TALSPEAK modeling calculations (I = 2.0 M, T = 25.0°C)
Values in parentheses are interpolated based on Figure 1.

Using the data analysis and plotting routines of HySS 2009¹, aqueous phase speciation plots (extraction equilibria were not considered) were developed for the lanthanides for a TALSPEAK-relevant aqueous medium comprised of 0.01 M DTPA, 2.0 M Na/HLac, I = 2.0 M, T = 25°C in the TALSPEAK operational pH range of 1-4 (figure 2) where speciation plots are shown for La³⁺ to Gd³⁺ and Yb³⁺. It can be seen that below pH 2 lanthanide lactate complexes dominate aqueous speciation. At the pH 4 upper limit of the plots LnDTPA²⁻ is the dominant species, though only just so for La³⁺; the increasing relative strength of lanthanide DTPA complexes from La³⁺ to Nd³⁺ actually account for the decline in extraction that is observed for these lanthanides in TALSPEAK. In the pH 2-4 region, the complexes Ln(Lac)_n³⁻ⁿ and LnDTPA²⁻ are competitive (within the constraints of the concentration limits selected). Based on the pH at which the LnDTPA²⁻ and Ln(Lac)₃ curves intersect, it is obvious that the competitive balance shifts increasingly toward Ln(DTPA)²⁻ from La³⁺ to Gd³⁺. The reverse shift toward a more competitive balance between 0.01 M DTPA and 2.0 M lactate seen in the Yb³⁺ curve is representative of the trend seen in the second half of the series, in which the DTPA holdback effect becomes less competitive with HDEHP extraction and the lanthanides heavier than Nd are successively extracted more strongly. This pattern arises because lanthanide lactate complex stability continues to increase across the series, while Ln(DTPA)²⁻ stability levels off for the ions heavier than Gd³⁺.

¹ HySS 2009 (Hyperquad Simulation and Speciation; Peter Gans, Protonic Software; <http://www.hyperquad.co.uk/hyss.htm>). This website also has a reference to the use of this software (Coordination Chemistry Reviews, 184 (1999) 311–318).

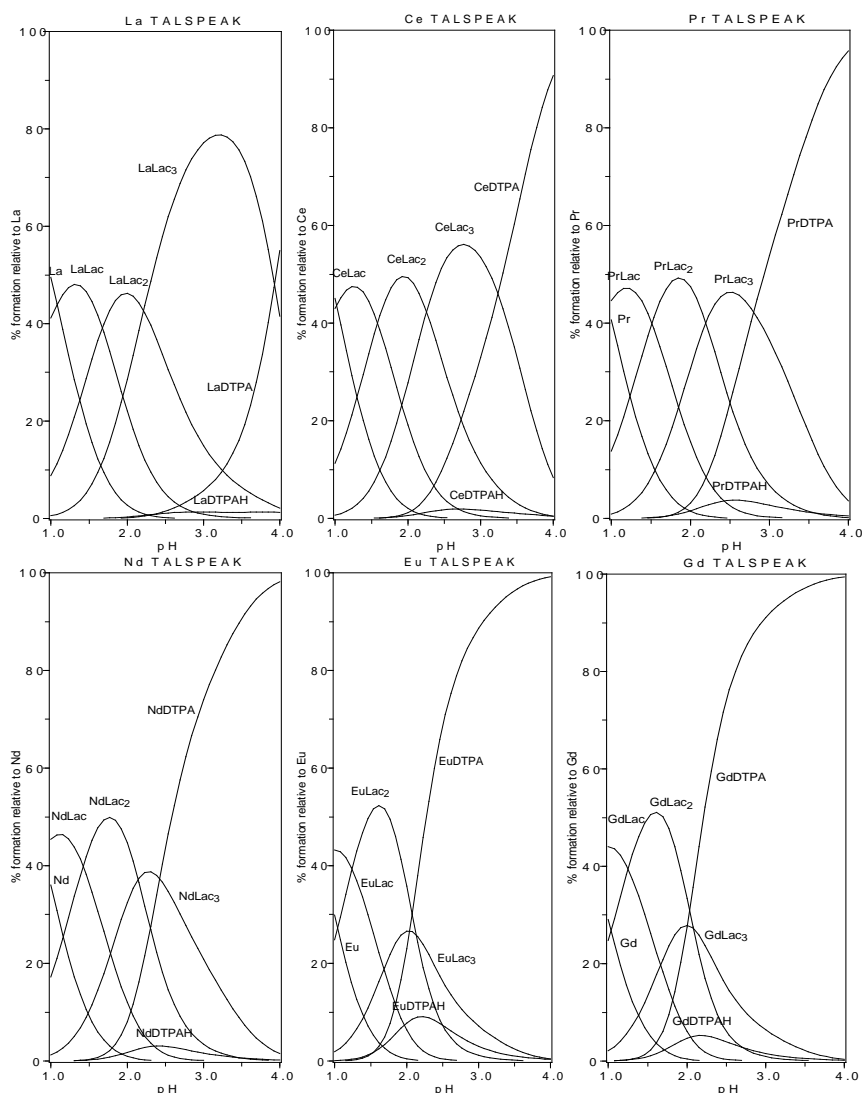


Figure 2. Predicted stability field diagrams for selected lanthanide DTPA and lactate complexes under TALSPEAK –relevant conditions ($[DTPA]_t = 0.01 \text{ M}$, $[Na/HLac] = 2.0 \text{ M}$, $T = 25^\circ\text{C}$, $I = 2.0 \text{ M}$, $[Ln^{3+}] = 0.001 \text{ M}$)

Speciation calculations assessing the relative stability of the $Eu \cdot DTPA^{2-}$, $Eu(HDTPA)^-$, and free DTPA ligand in 0.1 M KNO_3 , 2.0 M NaClO_4 and $2.0 \text{ M NaO}_3\text{SCF}_3$ indicate a somewhat diminished importance for the $Ln(HDTPA)^-$ complexes at 2 M ionic strength than at 0.1 M . Under TALSPEAK relevant conditions, it is seen that Ln-lactate and Ln DTPA complexes are competitive for the lightest and heaviest lanthanides (in the aqueous speciation), but in the middle of the series $Ln(DTPA)^{2-}$ is the dominant aqueous species.

In a titration microcalorimetry investigation, Grimes reported results that could only be interpreted to indicate that Eu DTPA complexes were weaker in 1.9 M lactate media than in 0.2 M lactate media (at constant 2.0 M ionic strength and temperature). This unexpected result points to a specific ion activity effect related to lactate solutions. Specific ion effects of this sort can compromise the accuracy of thermodynamic modeling predictions in aqueous media as complex as TALSPEAK aqueous phases. Furthermore, the balance between enthalpy and entropy in complexation reactions can provide useful insights into cation binding trends. To address this observation and to gain insights into the limits of titration calorimetry, experiments have been completed examining the thermochemistry of Ln-DTPA complex formation reactions.

The ΔH values for complexation of the rare earth metals by DTPA in 2.0 M NaNO_3 at 25.0°C are shown in Table 4. They are compared to results obtained previously^{39,40} at lower ionic strength. At either ionic strength, the complexation enthalpies of all lanthanides according to equation 6 (above) are exothermic. The ΔH values increase in magnitude from lanthanum through europium, level off through dysprosium, and decrease thereafter such that ΔH_{Lu} is similar to ΔH_{La} . The reaction becomes approximately 8-9 kJ/mol less exothermic as the medium is shifted toward infinite dilution at 0.1 M ionic strength. The difference in magnitude of ΔH_c between the middle lanthanides and those towards the ends of the series is more pronounced in NaClO_4 media than in the NaNO_3 media.

Metal	Ionic Strength		
	^a 0.1 M	^b 0.5 M	^c 2.0 M
	$\Delta H /$ kJ/mol	$\Delta H /$ kJ/mol	$\Delta H /$ kJ/mol
Y	-27 ± 0.4	-36.3 ± 0.3	-35.0 ± 0.6
La	-22 ± 1.6	-25.3 ± 0.4	-30.3 ± 0.2
Ce	-24 ± 1.6	-29.9 ± 0.3	-31.2 ± 0.2
Pr	-26 ± 0.8	-35.5 ± 0.3	-35.5 ± 0.5
Nd	-30 ± 0.4	-38.4 ± 0.5	-38.0 ± 2.0
Sm	-33 ± 0.8	-44.2 ± 0.4	-41.0 ± 1.0
Eu	-32 ± 0.8	-47.8 ± 0.4	-42.6 ± 0.5
Gd	-31 ± 1.2	-47.5 ± 0.4	-42.0 ± 1.0
Tb	-31 ± 0.4	-44.1 ± 0.3	-42.2 ± 0.2
Dy	-31 ± 1.2	-44.7 ± 0.5	-42.6 ± 0.2
Ho	-30 ± 0.4	-42.6 ± 0.4	-41.0 ± 0.6
Er	-30 ± 0.8	-41.3 ± 0.4	-39.7 ± 0.4
Tm	-26 ± 0.4	-36.6 ± 0.3	-37.7 ± 0.9
Yb	-25 ± 0.8	-34.9 ± 0.4	-34.6 ± 0.3
Lu	-21 ± 0.4	-32 ± 0.5	-30.8 ± 0.4

Table 4. Enthalpy values for the formation of $\text{Ln}\cdot\text{DTPA}^{2-}$ species in 0.1 M, 0.5 M, and 2.0 M ionic strength.

^a K^+ salt used as background electrolyte.(Choppin, G.R.; Goedken, M.P.; Gritmon, T.F. *J. Inorg. Nucl. Chem.* (1977) **39** 2025-2030) ^b NaClO_4 used as background electrolyte. (Moeller, T., Thompson, L.C. *J. Inorg. Nucl. Chem.* (1962) **24**, 499-510) ^c NaNO_3 used as background electrolyte (Johnson, Gabriel Eugene, Studies of the Thermodynamics of DTPA Complexation of the Rare Earth Elements at High Ionic Strength: Applications to the TALSPEAK Process, M.S. Thesis, Washington State University, August, 2012).

The ΔG_c values determined by potentiometric titration were combined with the ΔH_c values determined in the calorimetric experiments to calculate ΔS_c values, shown in Table 5. At 0.1 M and 2.0 M ionic strengths, a largely linear increase in ΔS is seen across the series. These are the same conditions under which the largest mid-series decrease was observed in ΔH for this reaction. As with ΔG and ΔH , dependence of ΔS on ionic strength at high supporting electrolyte concentrations is minimal, but ionic strength has an appreciable effect as supporting electrolyte concentration is lowered toward infinite dilution.

Metal	ΔS / J/mol·K	ΔS / J/mol·K	ΔS / J/mol·K	-T ΔS kJ/mol
Y	330	269 ± 2	268 ± 2	79.9 ± 0.6
La	298	264 ± 2	243 ± 1	72.4 ± 0.3
Ce	310	265 ± 2	260 ± 1	77.5 ± 0.3
Pr	314	257 ± 2	257 ± 2	76.6 ± 0.6
Nd	312	256 ± 2	261 ± 6	77.8 ± 1.8
Sm	315	248 ± 2	260 ± 5	77.5 ± 1.5
Eu	320	239 ± 2	260 ± 2	77.5 ± 0.6
Gd	322	238 ± 2	263 ± 3	78.4 ± 0.9
Tb	328	263 ± 2	263 ± 1	78.4 ± 0.3
Dy	332	254 ± 2	264 ± 1	78.7 ± 0.3
Ho	332	259 ± 2	273 ± 2	81.4 ± 0.6
Er	333	265 ± 2	277 ± 2	82.6 ± 0.6
Tm	345	284 ± 2	278 ± 3	82.9 ± 0.9
Yb	349	286 ± 2	285 ± 1	85.0 ± 0.3
Lu	357	290 ± 2	301 ± 1	89.7 ± 0.3

Table 5. Entropy values for the formation of Ln·DTPA²⁻ species in 0.1 M, 0.5 M, and 2.0 M ionic strength.

^aCalculated from ΔH and ΔG experiments where a K⁺ salt is used as background electrolyte (Choppin, G.R.; Goedken, M.P.; Gritmon, T.F. *J. Inorg. Nucl. Chem.* (1977) **39** 2025-2030).

^b Calculated from ΔH and ΔG experiments where NaClO₄ is used as background electrolyte. (Moeller, T., Thompson, L.C. *J. Inorg. Nucl. Chem.* (1962) **24**, 499-510)

^c Calculated from ΔH experiments where NaNO₃ is used as background electrolyte and ΔG experiments where NaClO₄ is used as background electrolyte (Johnson, Gabriel Eugene, Studies of the Thermodynamics of DTPA Complexation of the Rare Earth Elements at High Ionic Strength: Applications to the TALSPEAK Process, M.S. Thesis, Washington State University, August, 2012)

The pattern of increasing ΔG_{LnDTPA} from La to Eu in this series is arises from a changing complexation enthalpy while entropy must remain largely constant. From Eu-Dy both entropy and enthalpy remain nearly constant (thus the free energy is also constant). From Dy to Lu complexation enthalpies become steadily less exothermic while a compensating entropy increase compensates to maintain a stable free energy. It is not unreasonable to speculate that beyond Dy the decreasing size of the lanthanide ion combined with the comparative bulk of DTPA lead to reduced space for residual hydration of Ln(DTPA)²⁻ and a resultant increase in entropy resulting from the release of hydration sphere water molecules to the bulk.

The determination of lanthanide-DTPA complexation enthalpies at high ionic strength enabled a comparison of the observed enthalpies of the individual components of TALSPEAK with the observed net enthalpy of the process as determined by Nilsson previously. To do this, the individual enthalpies of each step in the series of reactions required to move a lanthanide ion from the aqueous phase to the organic phase were summed. This model starts with the lanthanide ion in a stable complex with DTPA in the aqueous phase. It is necessary (thermodynamically) to first de-complex the lanthanide from DTPA, then extract the lanthanide into the organic phase (releasing three protons per extracted metal ion), and finally to re-protonate DTPA⁵⁻ to H₃DTPA²⁻. The observed enthalpies for the DTPA decomplexation reaction, the HDEHP-facilitated phase-transfer reaction, and all relevant protonation and deprotonation reactions were

summed to obtain the heat of extraction one would expect in an ideal TALSPEAK system. The data used to construct the model for europium are provided as an example in Table 6. The ideal net reaction enthalpy was then compared to the experimentally determined enthalpy of the TALSPEAK process, in the case of Eu^{3+} showing a discrepancy of 27.7 kJ/mol for the europium extraction.

Stage	Reaction	$\Delta\text{H} / \text{kJ/mol}$
Breaking of EuDTPA^{2-} complex	$\text{EuDTPA}^{2-} \rightleftharpoons \text{Eu}^{3+} + \text{DTPA}^{5-}$	42.6 ± 0.5
Extraction to organic layer	$\text{Eu}^{3+} + 3(\text{HA})_{2,\text{org}} \rightleftharpoons \text{Eu}(\text{AHA})_{3,\text{org}} + 3\text{H}^+$	-13.1 ± 1.2
Reprotonation of DTPA^{5-}	$\text{DTPA}^{5-} + \text{H}^+ \rightleftharpoons \text{HDTPA}^{4-}$	-30.3 ± 0.1
	$\text{HDTPA}^{4-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{DTPA}^{3-}$	-24.6 ± 0.1
	$\text{H}_2\text{DTPA}^{3-} + \text{H}^+ \rightleftharpoons \text{H}_3\text{DTPA}^{2-}$	-9.8 ± 0.1
Calculated net extraction	$\text{EuDTPA}^{2-} + 3(\text{HA})_{2,\text{org}} \rightleftharpoons \text{Eu}(\text{AHA})_{3,\text{org}} + \text{H}_3\text{DTPA}^{2-}$	-35.2 ± 1.3
Experimental net extraction		-7.5

Table 6. Calculated enthalpy of an ideal TALSPEAK extraction of europium. The calculated enthalpy (hypothetical net extraction enthalpy) is the sum of the enthalpies of all reactions known to be involved in the process (dissociation of EuDTPA^{2-} complex, extraction of Eu^{3+} to the organic layer, and reprotonation of DTPA^{5-}). All experimental values were determined at 2.0 M ionic strength and 25°C.

As shown in Figure 6, the energetic discrepancy observed for the extraction of europium in an ideal system vs. an experimental system remains relatively constant across the entire lanthanide series. The similarity between the experimental enthalpies of the extraction reaction and the full system has previously been taken to indicate that the extraction step is the primary contributor to the heat evolved by the TALSPEAK process and that the DTPA decomplexation step is only a minor contributor. In light of the thermodynamic data produced by this study, it seems that the breakup of the MDTPA^{2-} complex must have a large effect on the overall enthalpy of a TALSPEAK extraction. This enthalpy contribution is apparently roughly compensated for by endothermic contributions from some unknown reaction or set of reactions. These reactions may be related to the poorly-understood behavior of the lactic acid/lactate buffer used in conventional TALSPEAK. It is quite conceivable that the missing heat represents a contribution from an endothermic heat of dilution unique to the solvent extraction system that was not present in the calorimetry experiments.

To continue our prior observations of the basic underlying chemistry of the TALSPEAK process, we investigated the possibility of supramolecular organization of solute and solvent molecules in this system using scattering techniques (neutron scattering in particular), conventional spectroscopies (IR, NMR), thermochemistry (i.e., calorimetry) and radioanalytical methods to profile the formation of molecular aggregates in the organic (and possibly of the aqueous phase) of TALSPEAK-relevant solutions. Such phenomena are of interest for their impact on phase

transfer processes, but from a practical perspective for their potential importance in preventing accidental criticality conditions. The neutron scattering studies will be particularly important in this connection. Our studies followed the methods promoted by the research of Chiarizia and coworkers at Argonne National Lab.

Subtask 1b Supramolecular Organization in TALSPEAK Extractant Phases Using SANS.

Neutron scattering techniques have been employed to define the supramolecular organization of extractant molecules and extracted complexes in solvent extraction systems. Using the unique properties of neutrons and introducing a deuterated contrast medium (e.g., xylene-d₁₀) provide an opportunity to reveal details about the organization of solute molecules in extractant solutions. Grimes and co-workers investigated the organization of HDEHP-based TALSPEAK systems using the methods and mathematics of Small Angle Neutron Scattering (SANS) focusing on some of the same systems investigated by Marie and co-workers. The neutron scattering experiments were conducted at the High Flux Isotope Reactor at Oak Ridge National Laboratory.

Lanthanide extracted complexes in TALSPEAK organic media appear to include the conventional 1:6 complex (Ln(DEHP·HDEHP)₃) at low concentrations of total metal ion, and at least one polynuclear complex with the apparent 2:2:4 (Ln:Lac:DEHP) stoichiometry as the lanthanide:HDEHP ratio drops below 1:6 (when lactate is available). The dominant form of free HDEHP in the presence of extracted lactic acid is the conventional dimer (HDEHP)₂, but there is enough HLac extracted to have an impact on [HDEHP]_{free}; some of the information on HLac extraction above suggests a possible terminal stoichiometry for extracted lactic acid of HLac·(HDEHP)₂₋₃ as an important species. Each of these species could be expected to contribute to the neutron scattering profile of TALSPEAK extractant phases.

Grimes et al. reported the results of neutron scattering experiments on extractant solutions (primarily HDEHP, but one sample contained HEH[EHP]) in deuterated xylene samples prepared for analysis by contact with buffered lactate solutions of increasing concentrations (Table 7). Parallel samples examined the influence of increasing concentrations of lanthanide ions (La, Gd, Yb taken to represent light, middle, and heavy members of the series) on the state of aggregation in TALSPEAK organic solutions. In the extractant samples equilibrated only with lactic acid, the ratio of HDEHP:HLac ranges from 200:1 down to 2.4:1 at the highest extracted lactate system. In the metal loaded samples, the ratio of metal:lactate averages near to 1 (except at the lowest lactate concentration) while the HDEHP:Ln ratios vary from a maximum near 30:1 down to 3:1 in sample La_{0.031}. The spectrophotometry, NMR and ESI-MS results point towards domination of metal speciation by Ln(DEHP·HDEHP)₃ at low metal loading and most lactate concentrations, shifting toward domination by Ln₂(Lac)₂(DEHP)₄ as the ratio of HDEHP:Ln drops below 6:1. Comparing samples HL_{1.0} (HDEHP) with HL_{1.0} (HEH[EHP]), the 50% greater extraction of lactate and 30 times higher water content of the HDEHP samples are notable.

sample [†]	extractant	Ln ³⁺	[HA,HB] [‡] , M	[Ln ³⁺] _{org} , M	[HLac] _{org} , M	[H ₂ O] _{org} , M [‡]
HA _{0.1}	HDEHP	—	0.1004	—	—	—
HA _{0.2}	HDEHP	—	0.2002	—	—	—
HL _{0.1}	HDEHP	—	0.2002	—	0.0005	0.043
HL _{0.5}	HDEHP	—	0.2002	—	0.0032	0.043
HL _{1.0}	HDEHP	—	0.2002	—	0.0095	0.06
HL _{2.0}	HDEHP	—	0.2002	—	0.0408	0.124
HL _{1.0}	HEH[EHP]	—	0.1992	—	0.006	0.002
La _{0.003}	HDEHP	La ³⁺	0.1004	0.003	0.0048	—
Yb _{0.005}	HDEHP	Yb ³⁺	0.1004	0.005	0.0049	—
Gd _{0.013}	HDEHP	Gd ³⁺	0.1004	0.013	0.0127	—
La _{0.023}	HDEHP	La ³⁺	0.1004	0.023	0.02	—
La _{0.031}	HDEHP	La ³⁺	0.1004	0.031	0.0265	—

Table 7. Organic Phase Samples Prepared for SANS Analysis at T = 22(±1)°C in p-Xylene-d₁₀.

[†] HA = HDEHP, HB = HEH[EHP], HL = Lactic acid, [‡][H₂O]_{org} for the Ln³⁺ metal systems was estimated to be 0.030 M for the scattering length density calculations.

The neutron scattering results were first analyzed considering the scattering particles to be spherical (Guinier analysis, TABLE 8²). As the neutron scattering results reflect most clearly the contrast between areas of concentration of ¹H atoms and ²H atoms, the dimensions of metal ions, oxygen, phosphorus and carbon are unimportant aside from the effect they each have on ordering the orientation of the hydrogen atoms of HDEHP (primarily) relative to the deuterium of the xylene diluents, i.e., they do not impact neutron scattering directly. The fits of the scattering curves produce an estimate of the average radius of the scattering sphere (of ¹H atoms), which is used to calculate a number density of scattering particles (M_w). From the analysis the simple model can be used to calculate the number of HDEHP monomers present in the average scattering particle (n_w).

² The reader is referred to the original report for the details of the mathematical treatment of SANS data by this approach.

sample [†]	$R_{\text{spherical}}, \text{\AA}^{\S}$	Mw, g/mol	n_w	$n_w \text{ calc}$
HA _{0.1}	6.7 ± 0.5	620.4	1.92 ± 0.23	-
HA _{0.2}	6.7 ± 0.4	647.8	2.01 ± 0.23	-
HL _{0.1}	6.8 ± 0.1	647.1	2.01 ± 0.23	2.1
HL _{0.5}	7.1 ± 0.1	659.4	2.06 ± 0.24	2.05
HL _{1.0}	6.9 ± 0.1	668.6	2.08 ± 0.24	2.14
HL _{2.0}	7.9 ± 0.2	847.4	2.65 ± 0.31	2.62
HL _{1.0,HB}	6.2 ± 0.1	576.7	1.86 ± 0.22	-
La _{0.003}	8.0 ± 0.2	857.7	2.66 ± 0.32	2.65 [#]
Yb _{0.005}	7.8 ± 0.3	871	2.70 ± 0.33	2.71 [#]
Gd _{0.013}	8.3 ± 0.2	1130	3.50 ± 0.42	3.49 [#]
La _{0.023}	16.6 ± 0.4	4075.3	12.64 ± 1.50	macro [%]
La _{0.031}	16.4 ± 0.5	5152.3	15.98 ± 1.52	macro [%]

Table 8. Summary of Guinier Analysis, Radius of Gyration, Weight Average Aggregation Number of HDEHP Extractant Samples in *p*-Xylene-d₁₀.

All uncertainties are reported at the 95% confidence level.[†] HA = HDEHP, HB = HEH[EHP]

[§] $R_{\text{spherical}}$ values calculated from R_g assuming spherical particles for HDEHP and HEH[EHP] aggregates.

[#] Calculated using equations 9-12, as explained in the text.

[%] macroscopic aggregates formed, speciation modeling not possible.

It is seen in Table 8 that (HDEHP)₂ is likely the primary scattering particle³ for samples HA_{0.1}, HA_{0.2} (samples not contacted with lactate buffer solutions) and HL_{0.1, 0.5, 1.0, 1.0,HB}. A 30% larger average scattering particle is indicated for HL_{2.0}, coinciding with a 1:5 ratio of [Lac]:[HDEHP] in the extractant solution. Assuming a simple two component model, a mass balance expression can be used to relate the size of the average scattering particle to these species:

$$n_w^{\text{calc}} = \frac{m^2 \cdot [\text{HLac}(\text{HDEHP})_m] + 2^2 \cdot [(\text{HDEHP})_2]_{\text{free}}}{[\text{HDEHP}]_{\text{tot}}} \quad (2)$$

where $[(\text{HDEHP})_2]_{\text{free}}$ represents all HDEHP not associated with lactic acid and m is the average HLac:HDEHP stoichiometry. Considering values of $m = 1-3$, the best fit was provided using $m = 3$ ($n_w^{\text{calc}}(\text{HL}_{0.1}) = 2.01$, $n_w^{\text{calc}}(\text{HL}_{0.5}) = 2.05$, $n_w^{\text{calc}}(\text{HL}_{1.0}) = 2.14$, $n_w^{\text{calc}}(\text{HL}_{2.0}) = 2.62$). At the highest $[\text{HLac}]_{\text{org}}$, the 0.2 M HDEHP solution is 0.041 M (HLac)·(HDEHP)₃/0.038 M (HDEHP)₂ or roughly 60% bound to lactic acid, 40% free dimer.

³ Maximum scattering is provided by HDEHP based on the H-atom count in the principal scattering entities, H₂O, H₅C₃O₃, H₃₅C₁₆PO₄ (the per-deuterated diluent is present at significantly greater abundance and provides scattering contrast).

In the metal containing samples, larger particles are seen and the complexes $\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_3^4$ and $\text{Ln}_2(\text{L})_2(\text{DEHP})_4$ must be considered (besides the HDEHP and Lac species. Three mass balance expressions must be accommodated to analyze the speciation:

$$[\text{Ln}]_{\text{t org}} = [\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_3] + 2\cdot[\text{Ln}_2(\text{L})_2(\text{DEHP})_4] \quad (3)$$

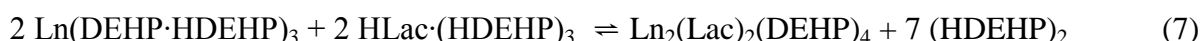
$$[\text{HLac}]_{\text{t org}} = [\text{HLac}(\text{HDEHP})_3] + 2\cdot[\text{Ln}_2(\text{Lac})_2(\text{DEHP})_4] \quad (4)$$

$$[\text{HDEHP}]_{\text{t org}} = 2\cdot[(\text{HDEHP})_2] + 3\cdot[\text{HLac}(\text{HDEHP})_3] + 6\cdot[\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_3] + 4\cdot[\text{Ln}_2(\text{Lac})_2(\text{DEHP})_4] \quad (5)$$

As above, HDEHP represents the primary scatterer of neutrons in these samples. Taking these relationships and species into account, the modified expression for a calculated n_w^{calc} when lanthanides are present would be:

$$n_w^{\text{calc}} = \frac{6^2 \cdot [\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_3] + 2^2 \cdot [(\text{HDEHP})_2]_{\text{free}} + 3^2 \cdot [\text{HL}(\text{HDEHP})_3] + 4^2 \cdot [\text{Ln}_2\text{L}_2(\text{DEHP})_4]}{[\text{HDEHP}]_{\text{tot}}} \quad (6)$$

In sample $\text{La}_{0.003}$, Guinier analysis indicates $n_w = 2.66 \pm 0.32$ for a sample containing 0.003 M La^{3+} , 0.0048 M HLac, 0.1004 M HDEHP. The fluorescence and NMR results suggest that $\text{La}(\text{DEHP}\cdot\text{HDEHP})_3$ should be the dominant metal complex in this lanthanide concentration range; iterative adjustment of the fit of the data to equation 12 (constrained by equations 9-11) results in $n_w = 2.65$ with partitioning of La between $\text{La}(\text{DEHP}\cdot\text{HDEHP})_3$ (70%) and $\text{La}(\text{Lac})_2(\text{DEHP})_4$ (30%). In samples $\text{Yb}_{0.005}$ ($n_w = 2.70 \pm 0.33$) and $\text{Gd}_{0.013}$ ($n_w = 3.50 \pm 0.42$), the metal ion partitioning is analogously 45% $\text{Yb}(\text{DEHP}\cdot\text{HDEHP})_3$ and $\text{Yb}(\text{Lac})_2(\text{DEHP})_4$ (30%) and $\text{Gd}(\text{DEHP}\cdot\text{HDEHP})_3$ (33%) and $\text{Gd}(\text{Lac})_2(\text{DEHP})_4$ (67%). Based on these analyses, 75% of the scattering particles are $(\text{HDEHP})_2$ in $\text{La}_{0.003}$ and $\text{Yb}_{0.005}$, 45% in $\text{Gd}_{0.013}$. With abundant lactate available, $\text{Ln}(\text{Lac})_2(\text{DEHP})_4$ becomes increasingly important as the metal concentration increases. In the $\text{Gd}_{0.013}$ sample the distribution of HDEHP among the projected species is 45% $(\text{HDEHP})_2$, 26% $\text{Gd}(\text{DEHP}\cdot\text{HDEHP})_3$, 17% $\text{Gd}_2(\text{L})_2(\text{DEHP})_4$, and 12% $\text{HL}(\text{HDEHP})_3$. A balanced organic phase equilibrium constant expression can be suggested to define the relationship between these species, as follows:



however, this single expression does not produce a single equilibrium constant value for the three systems tested, suggesting that perhaps additional reactions contribute. The results of the fitting exercise are summarized in Table 9.

⁴ Lumetta and coworkers have recently reported results from vapor pressure osmometry and radiometric slope analysis studies that have been interpreted to indicate that the predominant lanthanide complex in HDEHP solutions in n-dodecane is $\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_2(\text{DEHP})$. The primary difference between that work and the scattering results is the diluent, which may account for this apparent difference in complex stoichiometry. In the interpretation of the present results, earlier NMR, ESI-MS, and lanthanide fluorescence results provide convincing evidence for the correctness of the $\text{Ln}(\text{DEHP}\cdot\text{HDEHP})_3$ stoichiometry in the aromatic diluent used in the present work.

sample	n_w (Guinier)	n_w (fit)	[Ln(DHD) ₃] M	[Ln ₂ L ₂ D ₄] M	[HL(HD) ₃] M	[(HD) ₂] M
La _{0.003}	2.66 ± 0.32	2.65	0.0021	0.00045	0.0039	0.0743
Yb _{0.005}	2.70 ± 0.33	2.71	0.00225	0.00138	0.00215	0.0750
Gd _{0.013}	3.50 ± 0.42	3.49	0.00429	0.00436	0.00398	0.0453

Table 9. Iterative fit of speciation results derived from Guinier analysis data for samples La_{0.003}, Yb_{0.005}, Gd_{0.013} using mass balance relationships and expression defining the size of the average scattering particle considering Ln(DEHP·HDEHP)₃ (*Ln(DHD)*₃), Ln₂(Lac)₂(DEHP)₄ (*Ln₂L₂D₄*), HLac·(HDEHP)₃ (*HL(HD)*₃), and (HDEHP)₂ (*(HD)*₂) as the scattering particles.

For samples La_{0.023} and La_{0.031} much larger aggregation numbers are indicated thus it is reasonable to project that some degree of supramolecular ordering of these species is probable. Given the trends in the relative concentrations as the metal concentration increases, it is reasonable to assume that the dominant “monomer” species in these clusters is La₂Lac₂(DEHP)₄ and that the larger aggregates correspond to clusters of these species, each representing about four HDEHP monomer equivalents, perhaps [La₂Lac₂(DEHP)₄]₃₋₄.

The scattering results demonstrate that the dominant HDEHP species in the absence of metal ions is the hydrogen bonded dimer, (HDEHP)₂. Absent lanthanides, it appears that lactic acid is extracted as the 1:3 complex (HL·(HDEHP)₃). Scattering in samples containing up to 0.005 M lanthanides (prepared by extracting lanthanides from aqueous media containing 1.0 M buffered lactic acid) indicate that the dominant metal complex is Ln(DEHP·HDEHP)₃, but Ln(Lac)₂·(DEHP)₄ is also important. At 0.013 M extracted lanthanide, the scattering results indicate lower Ln:DEHP stoichiometry and larger scattering particles. At higher metal concentrations, the SANS results indicate large aggregates, the largest aggregates achieving a size equivalent to up to 20 HDEHP monomers as the primary scattering entity⁵. Analysis of particle shapes indicate best fits with a uniform oblate spheroid particle.

Subtask 1c. Advanced TALSPEAK Separations Using a Malonate Buffer System. Studies of conventional TALSPEAK illuminated in particular the role of the concentrated buffer in TALSPEAK performance. Among the possible alternatives to lactate, which appears to account for the steep acid dependence of conventional TALSPEAK, is malonic acid. The extraction behavior of lanthanides and americium has been evaluated under Advanced TALSPEAK conditions using malonic acid as the aqueous buffering agent. The extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) was used as an organic phase liquid cation exchanger in *n*-dodecane diluent, while *N*-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) served as the Am-selective aqueous holdback reagent. Extractions conducted from malonate media exhibit a pH profile that flattens as the concentration of malonate is increased up to 1.0 M malonate. This relatively flat extraction behavior from pH 2.5-4.0 is reminiscent of previous studies on *Advanced TALSPEAK* in lactate media. A comparison of the extraction kinetics with other carboxylic acid buffers as well as the effects of varying HEDTA, HEH(EHP), and malonate concentration indicate rapid extraction kinetics at pH 2.5, slowing with increasing pH. The efficiency of separation of Am from Eu is demonstrated in Figure 3. Separation efficiency is low below pH 2.5, indicating the limited effectiveness of HEDTA under these conditions. Separation factors above 100 are seen at pH 2.5-4.0; they are apparently nearly independent of malonate concentration.

⁵ There was no evidence of any tendency to form a second organic phase in any of these samples.

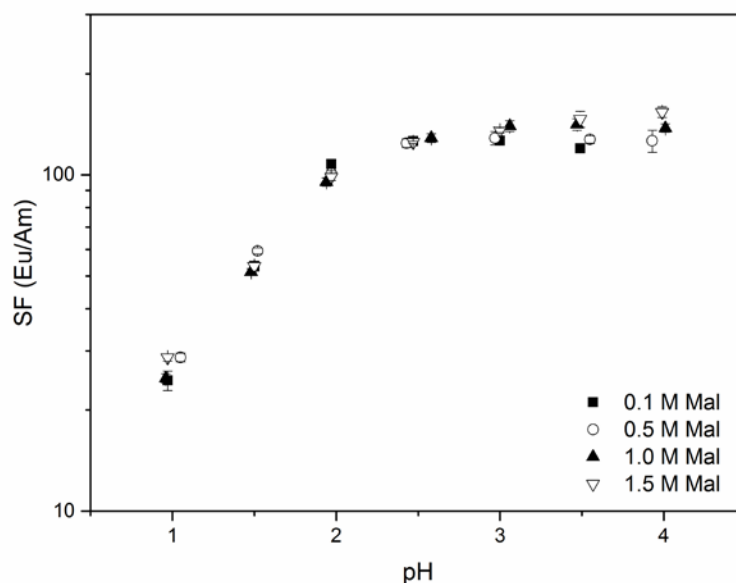
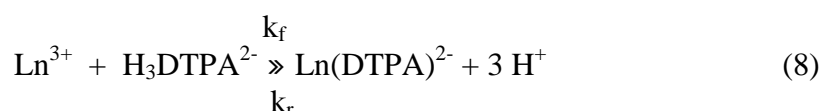


Figure 3: Separation factor of Eu and Am with 0.2 M HEH[EHP], 0.02 M HEDTA and varying malonate concentration.

Separations performed with HEDTA and HEH(EHP) in this buffer system exhibit fast phase transfer kinetics at lower pH values, while producing a relatively flat pH dependence of the distribution ratios (pH = 2.5-4.0) in studies with both trace metals and a highly metal loaded organic phase. This combination of properties suggests that malonate may offer advantages over previously studied carboxylic acids, such as lactic and citric acid, and thus is a promising candidate for inclusion in an Advanced TALSPEAK reprocessing plan. Extractions performed in malonate media suggest the presence of a ternary metal complex with HEDTA and malonate. Confirmation of this complex, its relative strength, and the role it plays in the extraction behavior of trivalent lanthanides and actinides will be discussed in a separate report.

Subtask 1d. Aqueous Complexation Kinetics in Conventional TALSPEAK. The nature of the phase transfer acceleration arising from increased concentration of the lactate buffer was examined in detail in a series of aqueous stopped-flow kinetics studies of lanthanide complexation kinetics in lactate buffer solutions. In these experiments, the total lactate concentration was held constant (in a given experiment) while the rate of displacement of lanthanide ions from a highly colored indicator complex was observed using spectrophotometric detection methods. Using this equilibrium perturbation technique, it was possible to determine rate constants for both the forward and reverse processes in the following reaction



The objective of this investigation was to provide a molecular scale explanation of the role of lactate ion in enhancing lanthanide phase transfer kinetics. The task is made challenging by the reality that, as DTPA is a much stronger complexant than lactate, the transparent lanthanide lactate complexes would never be observed directly, but could only be characterized by their effect on the rate of the Ln-DTPA reaction. Painstaking research on the patterns of reaction rates for the entire lanthanide series revealed that at pH 3.6 the rate of the complex formation reaction correlated in a linear fashion with the degree of lactate complexation in the medium of interest,

as shown below (Figure 4). The maximum rate for complex formation for both $\text{Ln}(\text{DTPA})^{2-}$ and $\text{Mn}(\text{EDTA})^-$ is seen to occur at Gd^{3+} ; this feature coincides with the observation of the lowest number of coordinated lactate molecules (Figure 4, right).

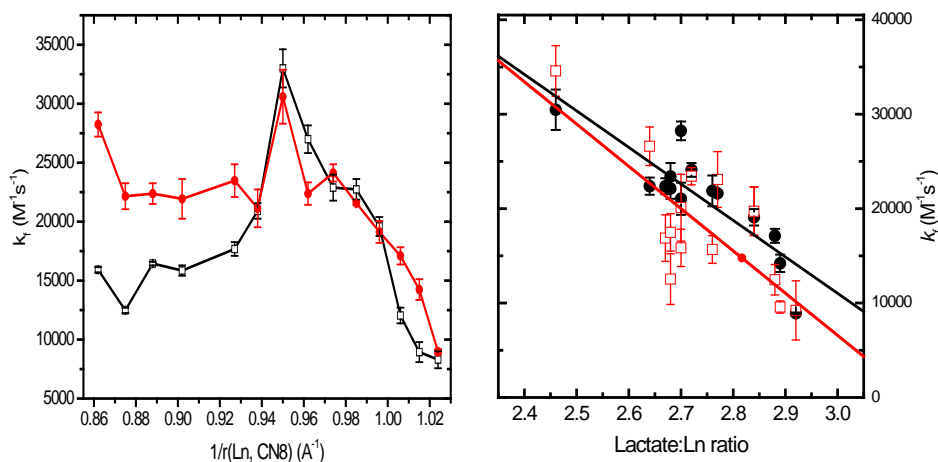


Figure 4. left: Correlation of complex formation rate constants across the Ln series with inverse cation radius at pH 3.6, 25 °C, and $[\text{Lac}_{\text{tot}}] = 0.3 \text{ M}$ (EDTA (\square), DTPA (\bullet)), **right:** Rate constant for formation of lanthanide EDTA and DTPA complexes in 0.3 M sodium lactate buffer, pH = 3.6, T = 25.0°C, I = 0.3 M as a function of the average equilibrium Lactate:Ln complex stoichiometry (\bar{n}_{LacLn}) (EDTA (\square), DTPA (\bullet)).

In this investigation, it was discovered that the reaction describing the complex formation reaction of LnDTPA^{2-} occurs under TALSPEAK conditions via the formation of an unidentified $(\text{Lac})\text{Ln}(\text{DTPA})^{x-}$ transient complex. At higher lactate concentrations the Ln-DTPA complex formation reaction slows. The activation entropy for this reaction is strongly positive, which is interpreted to require the dissociation of a lactate from a higher order $\text{Ln}(\text{Lac})_n$ species. This observation leads to the postulation of a chemical kinetics mechanism to describe Ln extraction as follows (considering only secondarily the influence of inter-phase transport reactions):



In this hypothetical reaction sequence, the first rate limiting process (reaction 9) is the release of the lanthanide cation from the thermodynamically stable $\text{Ln}(\text{DTPA})^{2-}$; this reaction is typically accompanied by rapid recombination reaction (reaction 10) and diffusion-controlled protonation

of DTPA⁵⁻ (reaction 11). Such reactions have been reported in the prior literature as being subject to catalysis by H⁺ and acetate buffer; the TALSPEAK-relevant work does not clearly establish H⁺ involvement, though lactate ion is certainly important. Reaction 11 is not rate-process relevant since these reactions occur rapidly and spontaneously at constant pH. The high concentrations of lactate anion in TALSPEAK drives the rapid formation of 1:1, 1:2, and 1:3 complexes (as dictated by equilibrium thermodynamics – the average ligand number varies across the series in a non-linear fashion).

The tris-lactate complex presents a moderately hydrophobic outer shell (assuming that each lactate is bidentate, the residual hydration is 2-3 water molecules) thus it can more readily diffuse toward the less polar interface double layer (reaction 15). In the interface, the de-dimerized HDEHP monomer exchanges its H⁺ to a lactate ion (reaction 16) and “drags” the Ln(Lac)₂(DEHP) deeper into the organic phase where the more abundant and more hydrophobic (HDEHP)₂ displaces the remaining lactate molecules forming the very stable and highly hydrophobic pseudo-octahedral Ln(DEHP·HDEHP)₃ complex (reaction 17). The ESI-MS, NMR, optical spectroscopy and SANS results indicate that more complex mixed ligand complexes become more important as the metal ion concentration increases to [Ln]:[HDEHP] ratios less than 1:6 (HDEHP monomer equivalents) at which point apparently polynuclear, mixed-ligand complexes become more important. In this analysis, the increased hydrophobicity of Ln(Lac)₃ and the lability (rapid ligand exchange) of these complexes would appear to represent a good combination for more rapid phase transfer kinetics.

By running several Eu-DTPA complexation experiments at different [Lac_{tot}] and adjusting the systems to have either constant pH or constant [Lac⁻] the roles of the species in the lactate buffer system in the complexation kinetics were also determined. The constant pH studies reveal that the rate constant of the complex dissociation reaction is directly dependent on [H⁺], while the constant [Lac⁻] systems showed that the rate constant of complex formation has an inverse first order dependence on [Lac⁻]. These two results provide evidence that [HLac] does not directly affect the complexation kinetics. Investigations of high [DTPA] under the condition of constant [Lac⁻] showed that the rate of complex formation eventually becomes independent of DTPA and in this region it is found that the rate is most significantly affected by the concentration of lactate ion.

The observation that the complexation rate between Eu³⁺ and DTPA in media of high concentrations of total lactate becomes independent of DTPA at high concentrations of the ligand has interesting implications with respect to the phase transfer kinetics in TALSPEAK. From the results obtained in the series of studies presented here a potential explanation for the accelerative effect of increased lactate concentrations on the extraction rate may be offered. At low concentrations of DTPA it was observed that the rate of complex formation between the ligand and Eu³⁺ is inverse first-order dependent on [Lac⁻]. At high concentrations of DTPA, where the rate becomes independent of [DTPA], the most significant effect on the complexation rate is obtained by changing [Lac⁻]. By increasing the lactate ion concentration a decrease in the rate of complexation is observed. In a TALSPEAK solvent extraction system the concentration of DTPA will be well within the complexation rate saturation range, and therefore the only way to significantly affect the aqueous complexation rate between the lanthanides and DTPA is by changing the lactate ion concentration. It was observed that pH only has a slight effect on the complexation rate under DTPA saturation conditions and mainly affects the dissociation rate of the complex.

As the pH of a TALSPEAK extraction system will be controlled for the best performance of the cation-exchanging extractant HDEHP, increasing the lactate ion will be achieved by increasing the total lactate in the system, which is seen to increase the rate of lanthanide extraction. This

effect can be explained in terms of the aqueous phase complexation kinetics. Starting with a Eu--DTPA system at equilibrium, the metal will be complexed by the ligand and non-extractable. Only when the metal dissociates from the ligand will it be extractable, and only if it is not re-complexed by another DTPA molecule. It has been observed in the previous studies of lanthanide complexation kinetics with DTPA in lactate media that there is a correlation between an increase in the average number of lactate ions coordinated to the lanthanide ion and a decrease in the Ln-DTPA k_f values across the lanthanide series.^{9,10} In media of high lactate ion concentrations when the lanthanide ion dissociates from DTPA, it will rapidly form lactate species with a Lac:Ln of 2:1 or 3:1. Although the Ln-lactate complexes do not compete with the thermodynamic stability of the Ln-DTPA complexes, the lactate complexes delay the re-complexation of the lanthanide ion by DTPA long enough to provide opportunity for the lanthanide to be extracted to the organic phase.

Additionally, the lactate ions coordinated to the lanthanide will be much more readily exchanged with an extractant molecule than the polydentate DTPA. Recent studies employing spectroscopic, luminescence, and thermometric experiments showed no formation of Ln-DTPA-Lac mixed complexes, at least not to a level detectable by those techniques. Given these observations the species interacting with HDEHP at the liquid-liquid interface are likely the Ln(Lac)₂⁺, Ln(Lac)₃, and Ln-DTPA complexes. As it is observed that the kinetics of HDEHP extraction from a Ln-DTPA system are slow which implies that the improved extraction kinetics are due to interactions between the Ln-lactate complexes and HDEHP at the interface. Increasing the total lactate concentration increases the prevalence of the Ln-lactate complexes, which slows the rate of formation of the Ln-DTPA complexes and in turn increases the rate of lanthanide phase transfer in TALSPEAK extraction systems.

To build on the lactate kinetics results and to link such investigations to our Advanced TALSPEAK ambitions to characterize malonate as a TALSPEAK buffer, this investigation was continued with a study of the mechanistic features of these same reactions in malonate buffer media, a potential alternative to lactate and citrate in Advanced TALSPEAK processes. Studying the complexation of lanthanides by DTPA in malonate buffered solutions allows the determination of the rate constants of the reaction at a time scale accessible by stopped-flow spectrophotometry. As in the lactate investigation, an auxiliary colored agent, Arsenazo III (AIII), was used to follow the decrease of the absorbance of Ln-AIII complexes while Ln-DTPA complexes are formed. The observed rate constant k_{obs} has shown a linear dependence to [DTPA] for light lanthanides (Ce³⁺ and Pr³⁺), while a saturation effect is observed at high [DTPA] for heavy lanthanides (Eu³⁺ to Lu³⁺), suggesting the formation of a precursor complex. Nd³⁺ and Sm³⁺ have an intermediate behaviour. It has been observed that k_f and K_{pre-eq} increase across the lanthanides series while k_d decreases at 25°C pH 2.5, I = 1 M, [Mal]_{tot} = 0.4 M.

Linear Free Energy Relationships (LFERs) have been found between thermodynamic data from literature and kinetics data of this work, showing that the driving force of the reaction is the balance between the interactions of malonate and DTPA with lanthanides. The determination of the activation parameters indicates a dissociative mechanism, in which Ln-Mal bonds break before DTPA complexes lanthanides. It also has been demonstrated that the intrinsic barrier mostly controlled the reaction kinetics, while the thermodynamic contribution could explained the difference between the lanthanides. The acid dependence experiments have made it possible to develop arguments that H₂DTPA³⁻ and Ln(Mal)₂²⁻ are the reacting species, which has been shown to be consistent with the ionic strength dependence experiments. Temperature studies have highlighted a dissociative mechanism due to positive entropy of activation. A mechanism involving different pathways consistent with these observations has been proposed, but not yet fully vetted. The difference observed between light and heavy lanthanides could be explained by an increase of the strength of interaction between lanthanides and malonate ions across the

lanthanides series. In the malonate system, a similar pattern of reactivity (to the lactate) is indicated by the appearance of saturation effects as pH increases and Ln-malonate complexes become more important (Figure5).

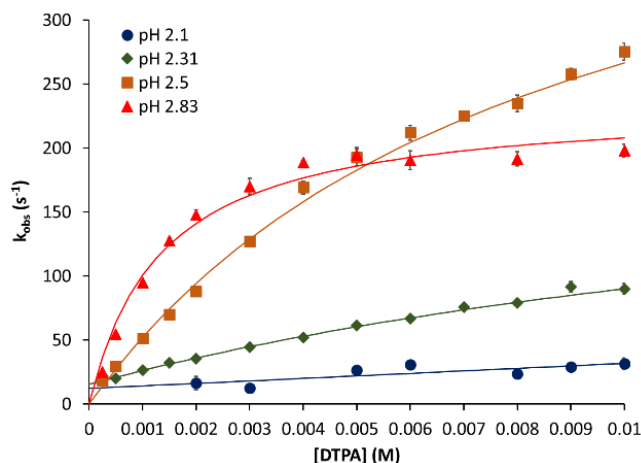


Figure 5. Dependence of observed reaction rate constant of Eu^{3+} on pH at 25°C and $[\text{Mal}]_{\text{tot}} = 0.4 \text{ M}$, $I = 1 \text{ M}$; $[\text{Eu}] = [\text{AAlII}] = 10^{-5} \text{ M}$. Lines represent the fits of the k_{obs} [DTPA] data.

Task 2. Profiling of the complexing kinetics and separations potential of DOTA (at elevated temperatures).

We believe that the comparatively low pK_a of the standard TALSPEAK extractant (bis-2-ethyl(hexyl)phosphoric acid – HDEHP) plays a role in the increasing mutual miscibility of the TALSPEAK phases, which plays a central role in the supramolecular organization of these solutions. We have investigated the effect of replacing HDEHP with less acidic phosphonic acid extractants and of the influence of added phase modifier solute molecules (like tributylphosphate - TBP) on supramolecular organization. These adjustments contributed to the development of the Advanced TALSEPAK process. We have also examined the potential for substituting 1,4,7,10-tetraazacyclododecane-*N, N', N'', N'''*-tetraacetic acid (DOTA, Figure 6) for DTPA in the TALSPEAK aqueous phase. Based on

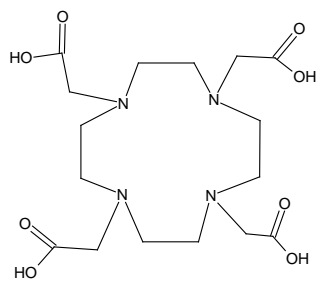


Figure 6. DOTA

earlier literature studies of DOTA complexes with lanthanides, we expect that complexation kinetics could still be an issue in this system. However, DOTA does contain one more soft donor nitrogen atom than DTPA and is structurally rigid, hence may be expected to exhibit enhanced Am/Ln separation efficiency at equilibrium.

Previous studies of the structure of lanthanide complexes in DOTA species indicate that the metal cation is perched between layers of four nitrogen and four oxygen donor atoms, not at the center of the tetraaza ring. On this basis, there is no intrinsic reason to expect it to be substantially slower kinetically than DTPA, as inversion of amine nitrogen atoms allows a more flexible arrangement of the O-donor atoms. There is no existing information on the stability of Am^{3+} or Cm^{3+} complexes with this ligand, so our investigation began with an estimate of the stability constants of Am^{3+} complexes with DOTA. In the experimental program, radioanalytical chemistry methods were supplemented by application of conventional analytical methods (spectrometric and thermometric methods combined with techniques designed to probe the interactions between solute molecules in organic solutions, e.g., NMR spectroscopy, light and

particle scattering methods, electrospray ionization – mass spectroscopy, interfacial tension). The ultimate objective of this Task was to gain improved understanding of the TALSPEAK Process and the role of supramolecular organization in complex solvent extraction systems.

Work on the characterization of N-donor complexants as reagents exhibiting selectivity for trivalent actinides and our studies of advanced approaches to doing TALSPEAK chemistry have convinced us that incorporating multiple-N-donor complexants into appropriately structured ligand architectures is a preferred pathway to efficient An/Ln separations. An example of this effect is the performance of DTPA in conventional TALSPEAK. We have previously studied the application of triethylenetetraaminehexaacetic acid (TTHA) as an alternative to DTPA in TALSPEAK, but found disappointing results suggesting that the fourth N-donor was not appreciably involved in cation coordination in acidic media. Motivated by the desire to bring four N atoms into a suitable geometry for this application, we examined the existing literature on heterocyclic polyaminopolycarboxylic acids as potential candidates for this application. These complexing agents are known to form strong complexes with lanthanides; there are no data on complexes with trivalent actinides. At first glance, these ligands are potentially problematic choices for application in hydrometallurgy because they are known to form substitution inert complexes and some degree of lability/reversibility is a requisite for hydrometallurgical separation system. With a generous donation from Dr. Judah Friese (Pacific Northwest National Lab) of several grams of 1,4,7,10-tetraazadodecanetetraacetic acid (DOTA), we were nevertheless encouraged to examine the potential of this system. Our modeling of lanthanide thermodynamics via a linear free energy analysis established that the Am/Nd separation potential was about 10^3 , as illustrated in Figure 7.

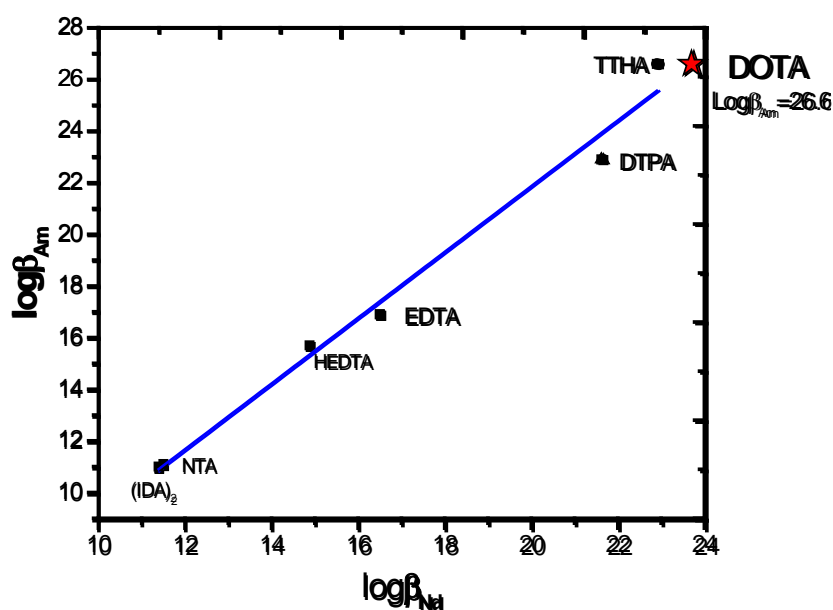


Figure 7. Linear free energy relationship, Am/Nd APCs

This analysis also established that the most effective approach would be to operate in the pH 4-5 regime, to match DOTA with the phosphinic acid extractant 2,3,4,4-trimethyl pentyl phosphinic acid (Cyanex 272) and to operate at elevated temperatures of 50-60 °C. Basic studies of aqueous complexation kinetics were complemented by solvent extraction studies to demonstrate Am-Eu separations. This work became the dissertation topic of Dr. Jessica Drader, who completed her studies late in 2012.

Reports from the prior literature established that lanthanide complexes with DOTA involved the initial formation of a doubly protonated $[\text{Ln}(\text{H}_2\text{DOTA})]^+$ intermediate that (at room temperature) slowly eliminated the H^+ ions to form the stable $[\text{LnDOTA}]^-$ complex. At room temperature and elevated pH this reaction takes days to come to completion. Not accepting the conventional wisdom explanation of H^+ -exchange-limited complex formation reaction, we examined the aqueous phase kinetics of this reaction in detail, operating at elevated temperatures (40-60 °C) and in acetate buffer media. We learned that in fact this system has an extremely large activation energy (E_a), resulting in a considerable increase in rates as temperature is raised. Equilibrium was reached at 60 °C in less than 30 minutes in many cases. We determined reaction rates for the entire lanthanide series employing Arsenazo III as an indicator of free Ln^{3+} to monitor the progress of the reaction via UV-Visible spectrophotometry.

We found that the reaction rate increased steadily across the lanthanide series, demonstrating an unexpected relative maximum at Tm (Figure 8). The literature explanation, credited to Wu and Horrocks, for the deprotonation reaction limited kinetics as arising from an OH^- - catalyzed reaction, to us does not seem credible in pH 4.5-5 media ($[\text{OH}^-] = 10^{-9} \text{ M}$). Instead our interpretation of these results is that the “settling in” of the lanthanide metal ion between coordination shells of amines and carboxylates is a more likely explanation, with Tm³⁺ representing the most favorable match between cation size/hydration and ligand steric requirements. A manuscript is in an advanced stage of preparation for submission to Inorganic Chemistry or the Journal of the American Chemical Society. Given the significant departure of our explanation from the existing wisdom, publication is proceeding with notable caution on our part.

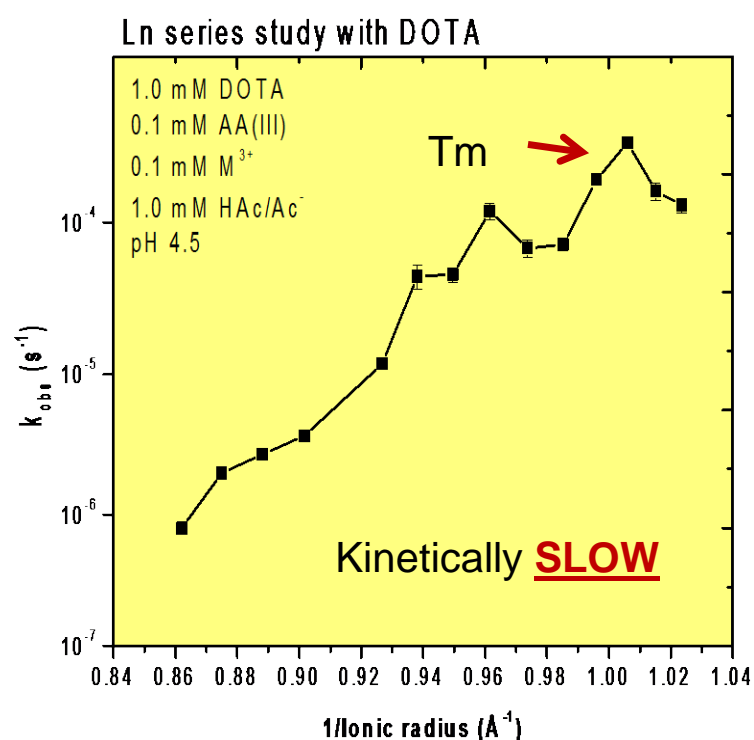


Figure 8. Lanthanide-DOTA complex formation rates by ligand displacement of Ln^{3+} complexes with Arsenazo III, T= 25.0 °C.

These reactions are not in a kinetic regime that would permit application of DOTA in a conventional TALSPEAK regimen. Nevertheless, we examined the comparative back extraction kinetics and equilibria for Am^{3+} , Eu^{3+} and Nd^{3+} partitioning between a Cyanex 272-dodecane solution and 0.1 M acetate buffer containing DOTA. Analysis of back extraction kinetics indicated a two stage back extraction regimen for Am^{3+} , the fast reaction taken to represent the effect of the formation of the $[\text{Am}(\text{H}_2\text{DOTA})]^+$ intermediate complex, the second corresponding to the relaxation of this intermediate into the $[\text{Am}(\text{DOTA})]^-$ thermodynamically stable species. This equilibration progresses over a period of several hours. At that time, Am^{3+} is more rapidly and more strongly stripped by DOTA, the 50 minute partitioning consistent with an Am/Nd separation factor of 500-1000, as predicted by the estimated Am stability constant and the linear free energy relationship. A publication for *Solvent Extraction & Ion Exchange* is in preparation describing these results.

In the final analysis, we have concluded that there is sufficient potential in this class of ligands to justify additional investigation. A logical next step is to examine in a similar sequence of studies the separations application potential of DOTA analogs with larger macrocycle rings, which should encourage faster kinetics while preserving the essential cation coordination environment. We are also considering amidation of DOTA for possible examination as an actinide-selective extractant. It is anticipated that this work will also be the subject of a search for additional funding to support further studies.

Task 3. Synthesis and characterization of N-donor extractant molecules.

Since the first report by Kolarik on the application of pyridine-1,2,4-bistriazine ligands (Figure 9) as potential actinide/lanthanide separation agents in the late 1990s, a considerable amount of

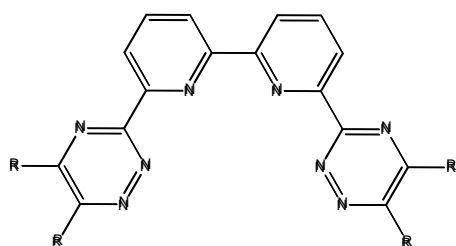


Figure 9. Bipyridine-1,2,4-bis triazine (BTBP)

research has been conducted seeking to develop this class of reagents to the task of direct extraction of trivalent actinides away from fission product lanthanides. In the French-led European program, many derivatives based on this structure have been synthesized and evaluated, with steady improvement in various properties of this class of ligands. To overcome instability

issues with respect to hydrolysis and radiolysis, various compromises have been made on the structure, some of which impact complexation kinetics. The development of an actinide-selective extractant system has much to recommend it, as the fundamental principle of extracting the minor component from the major component (Am and Cm from lanthanides in this context) carries obvious advantages in process efficiency. Our approach to this subject is to investigate the synthesis and separation potential of extractant molecules based on the functionalization of pyridine and bipyridine core functional groups with 1,2,3-triazole derivatives, as shown to the right.

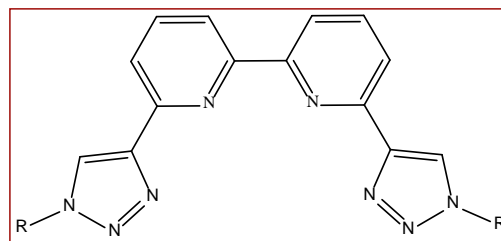


Figure 10. Bipyridine-1,2,3-bis-triazole (BTzBP)

Earlier work described in the Hoch dissertation focused principally on bidentate and tridentate variants of these structures, which are prepared using Sharpless “Click Chemistry”, in which the triazole rings are formed in a Cu(I)-catalyzed condensation reaction between alkyl azide molecules and aromatic nitriles. In that dissertation some effort was expended in characterizing

the thermal, hydrolytic and oxidative stability of several pyridine bis-triazole ligands. As compared with the extreme efforts expended to stabilize the 1,2,4 triazines, the 1,2,3 triazoles appear to exhibit substantially greater stability. Crystal structures establish that both pyridine and triazole nitrogen atoms participate in cation coordination, at least for first row transition metals. Various attempts at evaluation of the Am/Eu separation potential of these bi- and tridentate ligands pyridine mono- and di-pyrazoles gave disappointing performance. The decision was then made to focus on the preparation of bipyridine-bis-triazole derivatives (Figure 10), tetra N-donor ligands expected to function more aggressively in binding to lanthanides and actinides. Furthermore, the synthesis procedures for these ligands appear in general to be much simpler than that needed for the triazines.

This project continued in the capable hands of Postdoctoral research associate Dr. Julie Muller. Her initial efforts consisted of poring through the Hoch dissertation and research notes to develop efficient synthesis and improved purification procedures for the preparation of the di-decyl triazole derivative (Figure 11).

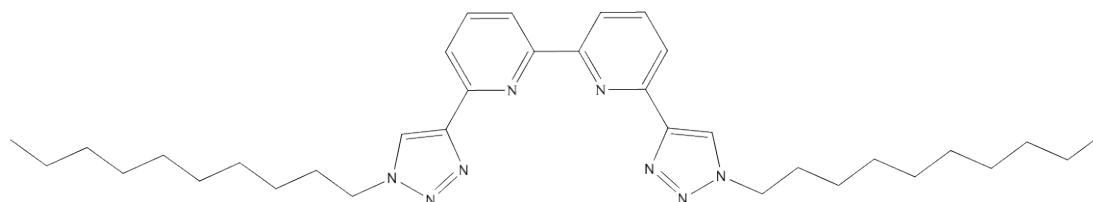
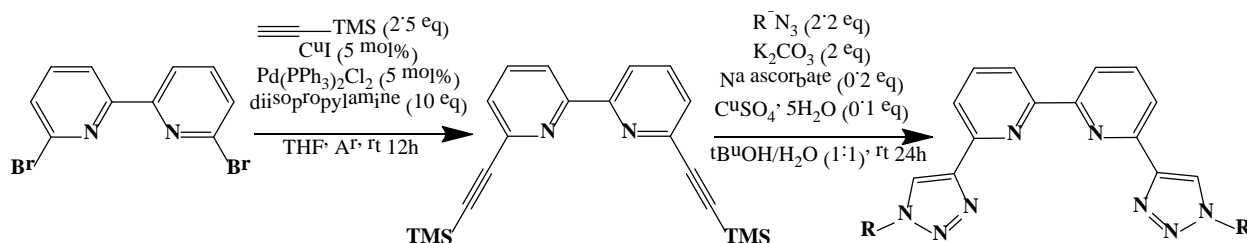


Figure 11. Didecyl bipyridinebistriazole

The very straightforward, two-step synthesis is:



This regimen easily achieves > 75% yields at each stage. Chromatographic purification produced sufficient quantities of the didecyl compound to enable characterization of its Ln/An separation efficiency. Surprisingly, the di-decyl bipy-bistriazole exhibited limited miscibility with all conventional solvent extraction diluents except chloroform, which while usable for such investigations is hardly ideal. Unfortunately, as a stand-alone extractant for extraction of Am or Ln from nitric acid media, this extractant proved ineffective. However, in a synergistic system combining the didecyl BTzDP and 2-bromodecanoic acid (as a co-extractant) combination achieves both extraction and Am/Eu separation efficiency, as demonstrated in Figure 12.

C_{10} -BTzBP 0.01 M + BDA 0.5 M in $CHCl_3$

$NaNO_3$ 1M at pcH 3

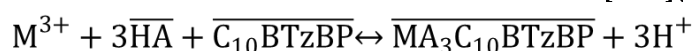
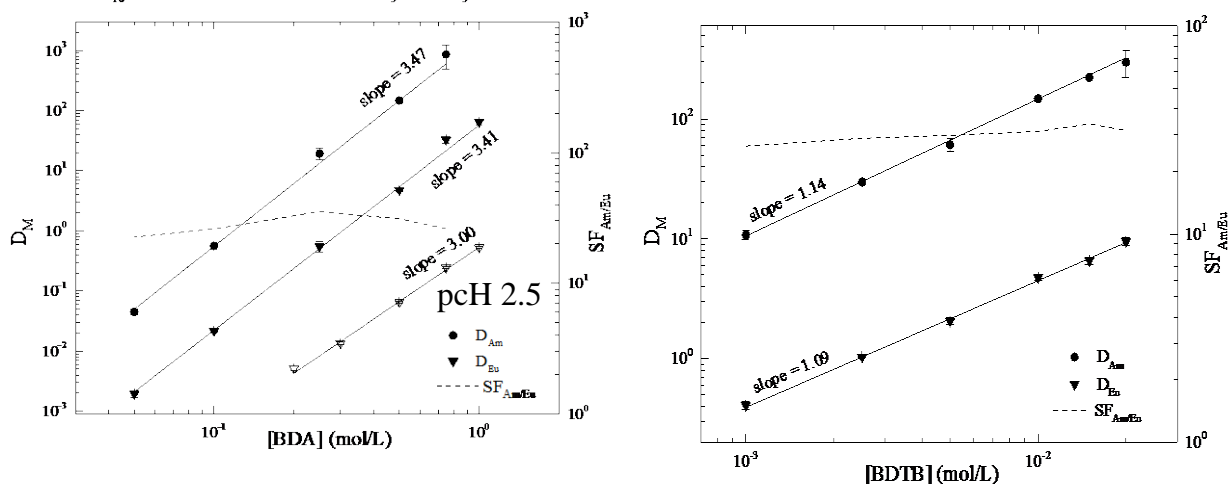


Figure 12. Extraction and separation of Am from Eu by C_{10} BTzBP and 2-bromodecanoic acid.

This far-from-optimum system achieves Am extraction, Am/Eu separation factors of 30-100 at pH 3, equilibrates rapidly with efficient phase separation and reasonable complex stoichiometries. Synthesis of additional derivatives designed to improve solubility in more acceptable diluents or to enable the formation of solids suitable for crystallographic characterization was initiated.

Work in the synthesis lab eventually produced a more suitable derivative of the BTzBP core. A novel N-donor extractant, 6,6'-bis(1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl)-2,2'-bipyridine (EH-BTzBP), was synthesized and tested for Am(III)/Ln(III) extraction and separation. EH-BTzBP in combination with 2-bromohexanoic acid (as lipophilic anion source) in toluene selectively extracts Am(III) from acidic solutions ($HNO_3 \leq 0.1M$) with Am(III)/Eu(III) separation factors of about 70. The complexation of Eu(III) with EH-BTzBP in methanol and toluene with or without presence of 2-bromohexanoic acid was studied by time-resolved fluorescence spectroscopy (TRFS). Both 1:1 and 1:2 complex species have been identified. Selected extraction results are shown in Figures 13 and 14. Phenyl derivatives were also produced to attempt the preparation of single crystals of f-element complexes. Samples of the latter were sent to Professor Albrecht-Schmitt at Florida State University for further study.

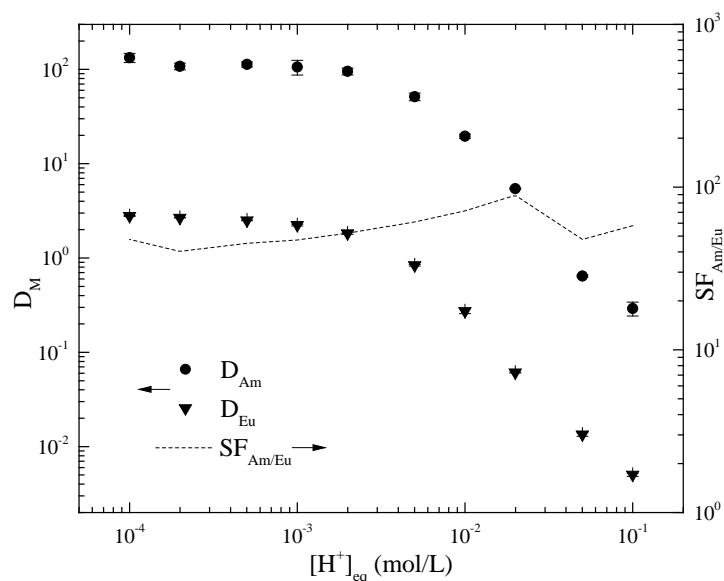
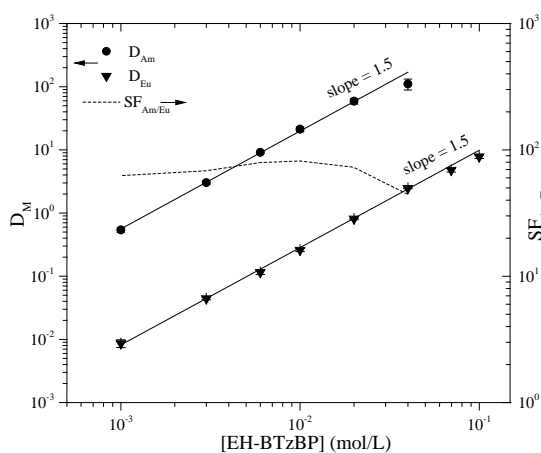
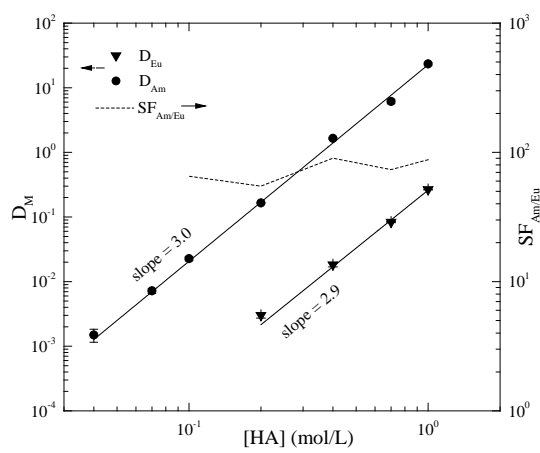


Figure 13: Extraction of Am(III) and Eu(III) as a function of acidity. Organic phase: C₁₀-BTzBP 0.01 M + 2-bromodecanoic acid 0.5 M in CHCl₃. Aqueous phase: Traces of ²⁴¹Am(III) and ¹⁵²Eu/¹⁵⁴Eu(III) in 1.0 M (H, Na, NO₃).



(a) Ligand dependence



(b) 2-bromohexanoic acid dependence

Figure 14: Extraction of Am(III) and Eu(III) as a function of EH-BTzBP or HA concentration. Organic phase: (a) EH-BTzBP + 1 M 2-bromohexanoic acid in toluene, (b) 0.01 M EH-BTzBP + 1 M 2-bromohexanoic acid in toluene. Aqueous phase: Radiotracer ²⁴¹Am(III) and ¹⁵²Eu/¹⁵⁴Eu(III) in 1.0 M (H, Na, NO₃) at pCh 2.

Slope analysis performed on the log [HA] vs. log D_M plot (Figure 14b) gave values of 3.0 ± 0.1 and 2.9 ± 0.1 for Eu and Am respectively. Three molecules or three dimers of 2-bromohexanoic acid must be involved in the extraction. Trans-lanthanide studies (Figure 15) indicate that the synergistic extraction system enables effective separation of Am from fission product lanthanides.

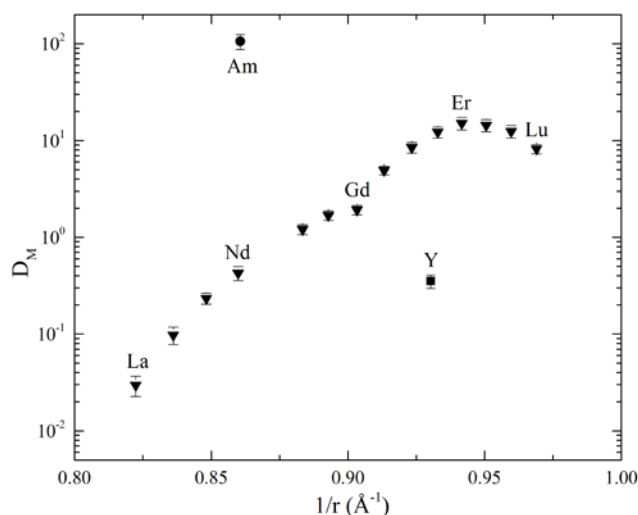


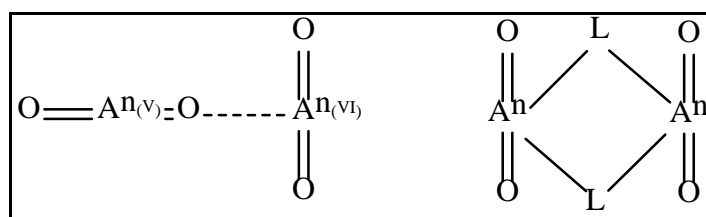
Figure 15: Extraction of the Ln(III) series, Y(III) and Am(III) as a function of their inverse ionic radii (CN = 9). Organic phase: 0.01 M EH-BTzBP + 1 M 2-bromohexanoic acid in toluene. Aqueous phase: 10^{-5} M of La-Sm and Eu-Lu + Y in 1.0 M (H, Na, NO_3) at pH 3, compared to Am(III) in the same conditions.

To summarize these results, extraction experiments performed on EH-BTzBP demonstrate that this new type of N-donor ligand used in combination with an acidic co-extractant may overcome several limitations of the BTP and BTBP extraction reagents. The extractant demonstrates high selectivity for An(III) over Ln(III), fast extraction kinetics, high solubility in non-polar solvents and resistance to acid hydrolysis and simulated radiolytic conditions. The complexation studies by spectrofluorimetry and UV spectrophotometry demonstrated the formation of 1:1 and 1:2 complexes between EH-BTzBP and lanthanides in methanol. Further TRFS studies on the Eu-EH-BTzBP complexes showed that the 2-bromohexanoic acid is not present in the first coordination sphere in methanol. Characterization of the complexes formed after extraction into toluene showed that both the 1:1 and 1:2 complexes are involved in the extraction. While EH-BTzBP has some drawbacks such as the need for the co-extractant 2-bromohexanoic acid (though there might be advantages accruing to the kinetics of phase transfer arising from the application of a cation exchanging co-extractant), the findings of this study can be utilized for further targeted synthesis of more suitable N-donor ligands for an An(III)/Ln(III) separation process.

Task 4. Characterization of pentavalent actinide cation-cation complexes.

Cation-cation complexes involving the interaction of pentavalent actinides (mainly Np(V)) were first reported by Sullivan and coworkers in 1961. These complexes are seen to result from interactions between AnO_2^+ ions and a variety of high charge density actinide (An(VI) and An(IV) (but not An(III)) and transition metal ions (Cr^{3+}). Because the complexes are weak, they are most readily observed in aqueous media of high ionic strength, in which water activity is significantly reduced. In aqueous systems, two different modes of interaction have been proposed for actinyl-actinyl complexes. The first involves the AnO_2^+ axial oxygen directly coordinating with the metal center of a hexavalent actinyl ion (AnO_2^{2+}). The second is that of the participation of two ligands bridging the AnO_2^+ and AnO_2^{2+} ions (see below). Both models proposed are consistent with vibrational spectroscopy and x-ray scattering measurements (An-An inter-nuclear distance is 4.2\AA) from solution and crystal, respectively. Such species have been implicated in some Np(V) solvent extraction reactions, but are of greatest interest in this program as a potential means of stabilizing pentavalent americium. Our investigations focused on application of electrochemical methods applied to U(VI) solutions and spectrophotometric

studies of Np(V), conducted with our INL collaborator, Dr. Leigh R. Martin and computational modeling. Dr. John Freiderich conducted the research at both WSU and INL. Four manuscripts are at an advanced stage of preparation based on this work.



Complexes between cations are important in a number of chemical equilibria. These complexes exist as electron transfer reaction intermediates, poly-nuclear hydrolysis products, and other ligand-bridged complexes, and dimer formation ($\text{NpO}_2^+ \text{-NpO}_2^+$). There is a comparative lack of information in the chemical literature that focuses on the systematic study of cation-cation complexes, particularly when considering actinyl-actinyl complexes. Our investigations of cation-cation complexes began with a study of the electrochemical reduction of U(VI) in aqueous media. Conditional equilibrium constants (K_{eq}) describing the interactions between oxidized actinide ions (actinyl-actinyl complexes) specifically relating to reversible, non-redox reaction: $\text{UO}_2^+ + \text{UO}_2^{2+} \rightleftharpoons [\text{UO}_2 \cdot \text{UO}_2]^{3+}$ in chloride and perchlorate aqueous media over a range of ionic strengths. Because UO_2^+ has limited stability with respect to disproportionation, this study was conducted using electrochemical techniques (cyclic voltammetry, normal pulse voltammetry, and chronocoulometry) in which UO_2^+ is created by reduction of UO_2^{2+} at the electrode surface. At higher ionic strengths, a change in the UO_2^+ solvation environment is indicated by the appearance of a second anodic wave (Figure 16). An ECE mechanism is proposed to understand the electrode-solution interface chemistry of these uranyl reactions. Figure 16 shows the increase in the current of $E_{\text{pa},1}$ as $E_{\text{pa},2}$ decreases. The shapes of these voltammograms are highly reproducible as a similar behavior is observed when v is changed from 900 mV s^{-1} to 50 mV s^{-1} and back to 900 mV s^{-1} . This reaction was investigated in various supporting electrolytes and equilibrium constants determined (Table 10).

System	μ (M)	K_{eq} (M^{-1}) ^a	System	μ (M)	K_{eq} (M^{-1}) ^a
CaCl ₂	1.2	5.3 ± 0.4	Mg(ClO ₄) ₂	1.2	----
	1.4	5.2 ± 0.4		1.4	----
	1.6	9.2 ± 0.7		1.6	----
	1.8	10.6 ± 0.6		1.8	----
	2.0	25.6 ± 1.5		2.0	14.9 ± 0.4
	2.6	25.1 ± 1.5		3.0	16.7 ± 0.8
	6.0	17.3 ± 0.8		6.0	13.9 ± 0.6
	9.0	9.3 ± 0.6		9.0	10.2 ± 0.2

^a: Errors reported are at the 95% confidence interval.

Table 10. $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ Complex as a function of ionic strength.

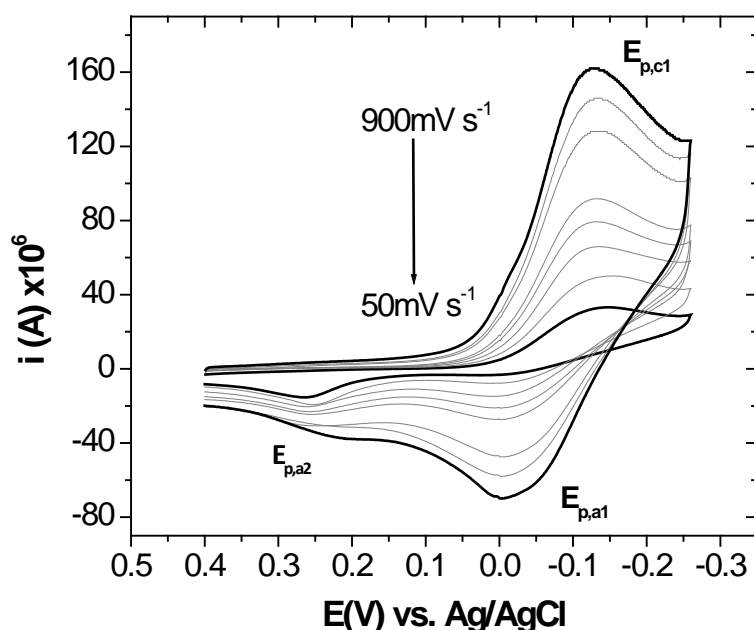


Figure 16. A decrease in v (0.900 V s^{-1} to 0.050 V s^{-1}) shows the emergence of the second anodic wave. Solution conditions: $[\text{UO}_2(\text{ClO}_4)_2] = 0.01 \text{ M}$, $\mu = 9.0 \text{ M}$ ($\text{Mg}(\text{ClO}_4)_2$), $[\text{HClO}_4] = 0.01 \text{ M}$.

It was shown in this study that electrochemical techniques may be used to determine thermodynamic parameters for $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complexes in aqueous media. For the first time electrochemical techniques were used to determine the stability of cation-cation complexes in aqueous media. A comparison between different actinyl-actinyl complexes has been done. The experimental results indicate that several factors play a role in the formation of cation-cation complexes. These include: ionic strength (lowering of water activity), basicity of the yl-oxygen of the donor actinyl cation, and the solvent structuring around the cations induced by background anions. $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complexes increase in stability when the ionic strength is increased regardless of the aqueous system. An increase in the water structure induced by background electrolytes increases the strength of actinyl-actinyl complexes. It was found that for the $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complex stability followed the trend: $\text{Cl}^- > \text{ClO}_4^-$ at lower ionic strengths. When comparing this data to literature the general trend for the strength of cation-cation complexes may be formulated: $\text{SO}_4^{2-} > \text{Cl}^- > \text{ClO}_4^-$, which follows the same trend for water ordering to disordering anions. The counter cation for the background electrolyte plays little, if any, role in complex formation other than to help lower water activity.

The second stage of the investigation focused on neptunium and was conducted under the direct supervision of Dr. Leigh Martin at the Idaho National Laboratory. The chemistry of the dioxocation, NpO_2^+ , has been studied in numerous chemical systems. Under certain conditions NpO_2^+ may form cation-cation complexes. There is a lack of literature data pertaining to the systematic study of the details of cation-cation complexes, especially when considering actinyl-actinyl complexes. In this portion of the investigation, spectrophotometry was used to determine the equilibrium constants of $\text{NpO}_2^+ + \text{UO}_2^{2+} \rightleftharpoons [\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ in NaNO_3 media. Specific ion interaction theory (SIT) was used to predict activity effects in these high ionic strength aqueous

systems. In addition, enthalpic and entropic contributions to the free energy of the $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ complex were investigated over a range of ionic strengths (1.74-6.35 M). Thermodynamic parameters as a function of ionic strength (developed using van't Hoff analysis of equilibrium constants determined as a function of temperature) are shown in Figure 17. Enthalpy values exhibit little variation with ionic strength. The complexes increase in strength with increasing ionic strength driven by an increasingly favorable entropy.

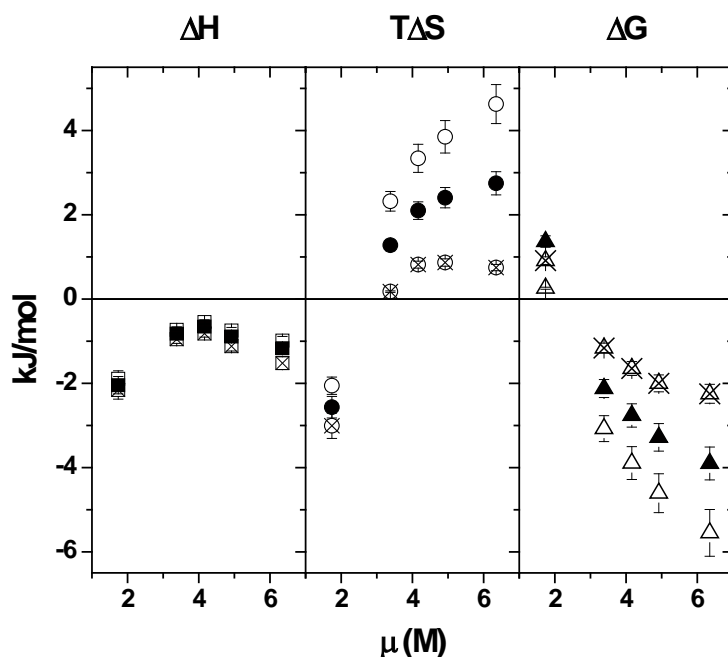


Figure 17. Enthalpic and entropic contributions to the free energy for the $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ complex as a function of ionic strength. Hollow symbols (\square) represent $\epsilon = 0.096$, solid (\blacksquare) represent $\epsilon = 0.046$ and crossed (\boxtimes) represent $\epsilon = -0.005$.

Overall, it has been shown that electrochemical and spectrophotometric techniques may be used to determine thermodynamic parameters for $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ and $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complexes in aqueous media. For the first time electrochemical techniques have been used to determine the stability of cation-cation complexes in aqueous media. A comparison between different actinyl-actinyl complexes has been done. The experimental results indicate that several factors play a role in the formation of cation-cation complexes. These include: ionic strength (lowering of water activity), basicity of the yl-oxygen of the donor actinyl cation, and the solvent structuring around the cations induced by background anions. Both $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ and $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complexes increase in stability when the ionic strength is increased regardless of the aqueous system. The $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ complex is weaker in general than the $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complex which correlates with basicity of the yl-oxygen and the ligand metal center. Finally, alteration of the water structure induced by background electrolytes increases the strength of actinyl-actinyl complexes. It was found that for the $[\text{UO}_2 \cdot \text{UO}_2]^{3+}$ complex stability followed the trend: $\text{Cl}^- > \text{ClO}_4^-$ and the $[\text{NpO}_2 \cdot \text{UO}_2]^{3+}$ complex followed the trend: $\text{NO}_3^- > \text{ClO}_4^-$ at lower ionic strengths. When comparing this data to literature the general trend for the strength of cation-cation complexes may be formulated: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$, which follows the same trend for water ordering to disordering anions. The counter cation for the background electrolyte plays little, if any, role in complex formation other than to help lower water activity.

Cation-cation complexes display a unique phenomenon, as two formally positive ions form “ion-pairs” in the solution when there are many other seemingly favorable options (i.e. water, anions, etc) that compete. In stage 3 of this investigation, we seized upon the inverse correlation between the activity of water and the strength of cation-cation complexes and extrapolated to the study of cation-cation interactions in polar organic media. In this stage, Np(V)-Lu(III) and Np(V)-Cr(III) cation-cation complexes in mixed-solvent media were examined (Figure 18 is representative of the Np(V)-Cr(III) complex). In Figure 18, a Np(V) spectrum demonstrating a Np(V)-Cr(III) complex in acetonitrile is shown. CrCl₃ in acetonitrile is purple in color, which is much different than the green color observed in aqueous solutions (Cr(H₂O)₆³⁺). Upon addition of the Np(V) stock to the acetonitrile/Cr³⁺ solution, the color changes immediately to green. Fits of Np(V)-Cr(III) spectrophotometric data indicates that complex stability constants increase from $K_{eq}([NpO_2 \cdot Cr]^{4+}) (M^{-1}) = 2.6$ (I=8 M, H₂O), to 62 ($X_{EtOH} 0.84/ X_{H_2O} 0.16$), to 3.2×10^8 ($X_{AN} = 0.78/X_{H_2O} = 0.22$). The apparent remarkable enhancement in stability of this complex in non-aqueous polar media is remarkable.

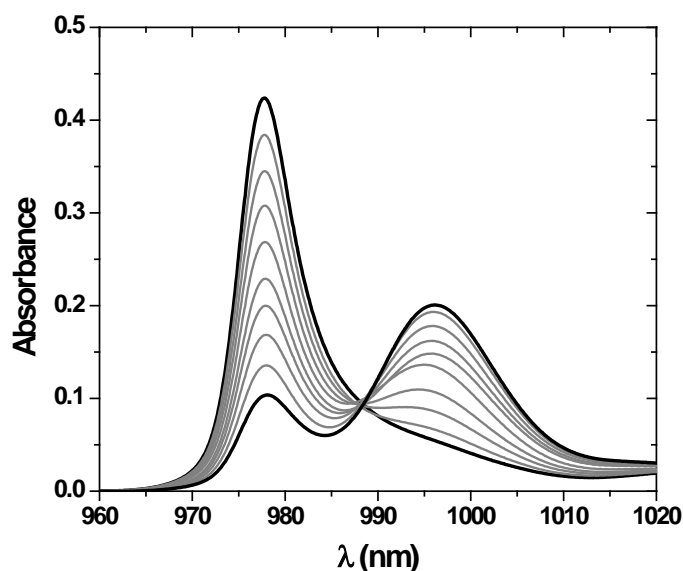


Figure 18. Absorption spectra showing complexation of Cr³⁺ by NpO₂⁺ to form a cation-cation complex in acetonitrile. Solution conditions: [NpO₂⁺] = 2 mM, [Cr³⁺] = 0.8 – 8 mM, 5 M H₂O, 25 °C.

The thermodynamics of complex formation and the driving forces leading to the formation of these two $[NpO_2 \cdot M]^{4+}$ complexes were emphasized in this portion of the study. The $[NpO_2 \cdot Cr]^{4+}$ complex demonstrates the following stability trend as the mixed-solvent changes: acetonitrile/water \gg 2-propanol/water \approx ethanol/water $>$ methanol/water \approx water. This trend is qualitatively explained by the free energy of transfer (ΔG_{tr}^{\ominus}) of binary salts, which observation may eventually assist in the understanding of cation-cation complex formation in mixed-solvent media. It has also been determined that NpO₂⁺ disproportionation in acetonitrile/water (Figure 19) is at least partially suppressed by formation of a cation-cation complex with Cr³⁺. This combination represents an interesting mixed-solvent/metal system that could stabilize actinides in higher oxidation states.

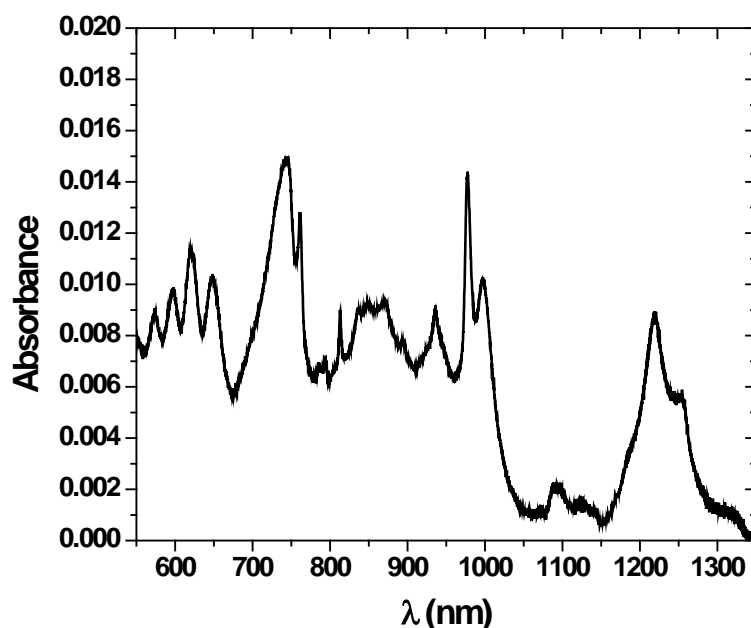


Figure 19. Absorption spectra showing the disproportionation of NpO_2^+ to Np^{4+} and NpO_2^{2+} in an acetonitrile/5 M H_2O matrix. In addition, the formation of a cation-cation complex is observed at 996 nm.

The tendency of NpO_2^+ to disproportionate in water/acetonitrile was successfully mitigated in a water/acetonitrile mixture through the addition of Cr^{3+} . The cation-cation complex $[\text{NpO}_2 \cdot \text{Cr}]^{4+}$ follows the general trend of stability as the solvent changes: acetonitrile \gg 2-propanol \approx ethanol $>$ methanol \approx water. While this stability trend does not correlate with the dipole moment of the solvent molecule or the dielectric constant of the medium, it does correlate with the solvent structuring effects of each different solvent, at least for the protic polar solvents. The strength of the $[\text{NpO}_2 \cdot \text{Cr}]^{4+}$ complex may be explained as a result of the weaker metal-acetonitrile interaction. This allows the NpO_2^+ dioxocation to interact more readily with the Cr^{3+} metal center. A $[\text{NpO}_2 \cdot \text{Lu}]^{4+}$ complex was observed in 2-propanol/water media. Overall this study, coupled with literature reports, indicates that by changing the solvent the stability of cation-cation complexes may be effectively increased and higher oxidation states of the actinides may be stabilized through cation-cation complexation in solvent systems that normally do not support these oxidation states.

Summary. In the conduct of this investigation, we have advanced understanding of TALSPEAK chemistry, helping to enable Advanced TALSPEAK options, increased understanding of pentavalent actinyl cation-cation complexes, introduced a new class of tetraaza extractant molecules for An(III)/Ln(III) separations, explored the potential for separations application of cyclic polyaminopolyacetate complexants like DOTA, and completed the first identification of U(V)-U(VI) cation-cation complexes using electrochemical methods. In the course of this work five new Ph.D. scientists have entered the workforce, with additional students still in the process. Research results were reported orally or in poster format in nearly 40 public presentations. Nine written reports have been published and an additional nine are in progress (at least). The young people who participated in this research have to a person become eager advocates for nuclear energy and responsible radioactive waste management. Finally, this extended investigation has led to the development of numerous fresh ideas for additional work.