FINAL REPORT

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Basic Energy Sciences

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"Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Fuel Cycle"

To:

Washington State University

PI: Sue B. Clark

FINAL REPORT: Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Fuel Cycle

U.S. Department of Energy, Basic Energy Sciences, Heavy Elements Program

Grant Number: DE-SC-0004102

PI: Sue B. Clark, Chemistry Department, Washington State University

Abstract:

The goal of this project has been to define the extent of hydration the f-elements and other cations in mixed solvent electrolyte systems. Methanol-water and other mixed solvent systems have been studied, where the solvent dielectric constant was varied systematically. Thermodynamic and spectroscopic studies provide details concerning the energetics of complexation and other reactions of these cations. This information has also been used to advance new understanding of the behavior of these cations in a variety of systems, ranging from environmental studies, chromatographic approaches, and ionization processes for mass spectrometry.

Summary of Contributions Resulting from this Grant:

Because of the electrostatic nature of the f-elements in solution, many of their complexation reactions in water are enthalpic, but yet favorable because of the entropy gain arising from desolvation of the hydration shell about the f-element cation. While the thermodynamics of fully aqueous systems are generally well studied, little was known about the impact of solvent additives prior to this work. At the same time, mixed solvent systems are frequently used to improve chromatographic separations, facilitate phase transfer in liquid-liquid and liquid systems, and enhance ionization for mass spectrometry. In addition, effluents contaminated with actinides and fission products that have been released to the environment often are sometimes composed of mixed solvents.

In this work, we have used experimental and computational approaches to quantify the impact of miscible non-aqueous solvents such as methanol on the thermochemistry of f-element complexation by carboxylic and alpha-hydroxy carboxylic acids. Most of these basic studies have involved the trivalent f-elements, and this work has also been benchmarked against similar studies involving cations of lower charge density, such as sodium. The presence of methanol tends to affect the entropy term for complexation by alpha-hydroxy carboxylic acids in previously unpredictable ways. As a result of this work, that impact is now quantifiable in many systems.

In addition to these very fundamental studies, we have extended this work to include use-inspired basic research on environmental transport, chromatographic separations, and ionization for mass spectrometry. Solvent dynamics clearly impact the migration of the f-elements in the environment. In addition, solvent dynamics can dominate the efficacy of ionization using

approaches such as electrospray prior to mass spectrometry, and the interactions of ions with ion exchange resins for chromatography.

Impact of New Knowledge Resulting from this Grant:

Possible changes to the civilian US nuclear energy program include plans to close the fuel cycle by (1) separating uranium for disposal as low activity waste, (2) recycling plutonium into mixed oxide (MOX) fuel, and (3) transmuting some of the long-lived actinides into less problematic isotopes for disposal. Successfully achieving such a fuel cycle requires unprecedented molecular control where the chemistry is orchestrated at the nanoscale. The new knowledge resulting from this grant begins to provide the foundation needed to enable the molecular control for separations in advanced fuel cycles.

Peer-reviewed Publications:

"Structural and Thermodynamic Properties of the Cm-III Ion Solvated by Water and Methanol"; Kelley, Morgan P.; Yang, Ping; Clark, Sue B.; Clark, Aurora E.; INORGANIC CHEMISTRY; 55:10; 4992-4999; DOI: 10.1021/acs.inorgchem.6b00477; Published: MAY 16 2016

"Characterization of Actinides Complexed to Nuclear Fuel Constituents Using ESI-MS"; McDonald, Luther W.; Campbell, James A.; Vercouter, Thomas; Clark Sue B.; ANALYTICAL CHEMISTRY; 88:5; 2614-2621; DOI: 10.1021/acs.analchem.5b03352; Published: MAR 1 2016

"Further structural analysis of Cr(III) oligomers in weakly acidic solutions"; Zhang, Zhicheng; Clark, Sue B.; Rao, Linfeng; Puzon, Geoffrey J.; Xun, Luying; POLYHEDRON; 105; 77-83; DOI: 10.1016/j.poly.2015.12.041; Published: FEB 17 2016

"Structure and Dynamics of NaCl Ion Pairing in Solutions of Water and Methanol"; Kelley, Morgan; Donley, Amber; Clark, Sue; Clark, Aurora; JOURNAL OF PHYSICAL CHEMISTRY B; 119:51; 15652-15661 DOI: 10.1021/acs.jpcb.5b07492; Published: DEC 24 2015

"Mechanical environmental transport of actinides and Cs-137 from an arid radioactive waste disposal site"; Snow, Mathew S.; Clark, Sue B.; Morrison, Samuel S.; Watrous, Matthew G.; Olson, John E.; Snyder, Darin C.; JOURNAL OF ENVIRONMENTAL RADIOACTIVITY; 148; 42-49; DOI: 10.1016/j.jenvrad.2015.06.009; Published: OCT 2015

"Integrated Computational and Experimental Protocol for Understanding Rh(III) Speciation in Hydrochloric and Nitric Acid Solutions"; Samuels, Alex C.; Boele, Cherilynn A.; Bennett, Kevin T.; Clark, Sue B.; Wall, Nathalie A.; Clark, Aurora E.; INORGANIC CHEMISTRY; 53:23; 12315-12322; DOI: 10.1021/ic501408r; Published: DEC 1 2014

"ITP of lanthanides in microfluidic PMMA chip"; Cong, Yongzheng; Bottenus, Danny; Liu, Bingwen; Clark, Sue B.; Ivory, Cornelius F.; ELECTROPHORESIS; 35:5; 646-653; DOI: 10.1002/elps.201300382; Published: MAR 2014

"Failure of ESI Spectra to Represent Metal-Complex Solution Composition: A Study of Lanthanide-Carboxylate Complexes"; McDonald, Luther W.; Campbell, James A.; Clark, Sue B.; ANALYTICAL CHEMISTRY; 86:2; 1023-1029; DOI: 10.1021/ac401751r; Published: JAN 21 2014

"Electroanalytical chemistry of lanthanides and actinides"; Schumacher, Paul D.; Doyle, Jamie L.; Schenk, James O.; Clark, Sue B.; REVIEWS IN ANALYTICAL CHEMISTRY; 32:2; 159-171; DOI: 10.1515/revac-2012-0032; Published: MAY 2013

Awards and Honors:

Sue B. Clark received the 2012 Francis P. Garvan-John M. Olin Medal of the American Chemical Society for her seminal contributions in actinide solution chemistry (which were supported by Basic Energy Sciences, Heavy Elements Program, including this grant) and her tireless efforts to train the next generation of radiochemists.

Morgan P. Kelley, a WSU Chemistry Graduate Student who is co-mentored by Sue B. Clark and Aurora E. Clark, was awarded a DOE Office of Science Graduate Student Research (SCGSR) Program in 2015. Using this support, he collaborated with Ping Yang of Los Alamos National Laboratory to develop ab-initio molecular dynamics descriptions of ion solvation in mixed solvent systems.

Mathew S. Snow, a WSU Chemistry Graduate Student who was mentored by Sue B. Clark, was awarded Department of Homeland Security Nuclear Forensics Graduate Fellowship that supported his PhD research. As a NFG fellow, he completed part of his PhD research in residence at Idaho National Laboratory.

PhD Theses by WSU Chemistry Graduate Student Support resulting from support (full or partial) by this Grant:

Morgan P. Kelley, 2016; "Experimental and computational studies on the hydration of f-element cations in mixed solvent systems"

Kevin T. Bennett, 2016; "Rapid estimation of actinide complexation constants in mixed solvent media"

Samuel S. Morrison, 2015; "Activation product analysis in the presence of fission products"

Amber S. Donley, 2014; "Solvent effects on the energetics of complexation reactions in binary aqueous methanol solutions"

Jamie L. Doyle, 2014; "Optimization of the electrochemical pre-concentration of f-elements"

Luther W. McDonald, 2013; “Using Electrospray Ionization, Mass Spectrometry to observe metal, complexant species relevant to the nuclear fuel cycle”

PhD These by WSU Chemistry Graduate Students who worked on aspects of this project, and funded by other sources:

Paul D. Schumacher, 2011; “An investigation into the pre-concentration of trivalent f-elements in aqueous solutions via electroanalytical techniques”. Supported by the US Army.

Mathew S. Snow, 2014, “Detection of the actinides and cesium from environmental samples”. Supported by the Department of Homeland Security, Domestic Nuclear Detection Office.