2003
DOE Separations and Heavy Element Chemistry Contractors' Meeting

Santa Fe, April 28-30, 2003

Sponsored by
The U.S. Department of Energy
Office of Basic Energy Sciences

Chemical Sciences, Geosciences and
Biosciences Division

Workshop Chairs:
John Miller, Lester Morss, and Norman Edelstein

Program and Abstracts

Contractors' Meeting
Heavy Element Chemistry Program
Separations Program

Hilton of Santa Fe
100 Sandoval Street
Santa Fe, New Mexico
April 28 – 30, 2003

Chemical Sciences, Geosciences and
Biosciences Division
Office of Basic Energy Sciences
Office of Science
Department of Energy

FOREWORD

This abstract booklet provides a record of the fifth U.S. Department of Energy (DOE) contractors' meeting in separations sciences and the second in heavy element chemistry. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry and separations sciences for over fifty years. Although these are distinct disciplines, they have much in common for many reasons, in particular because (1) separations research is needed to produce pure heavy-element samples and (2) heavy element chemistry provides the basis for many separations processes. Therefore, this year it was decided to hold these meetings jointly.

There is wide agreement that a gathering of researchers with common interests and sponsorship provides a fruitful environment to present and to exchange information about researchers' activities, to build collaborations among research groups with mutually reinforcing strengths, to identify needs of the research community, and to focus on areas for future research directions. The primary means of communicating research achievements and perspectives at this meeting is via posters and the discussions that illuminate the poster sessions. Groups of brief oral presentations serve to highlight the corresponding posters that follow each oral session. We have organized the agenda so that papers in related disciplines – such as spectroscopy, theory, and coordination chemistry – are loosely clustered together. We emphasize the informal nature of this meeting – it is not a review of researchers' achievements or future directions.

We are pleased to have the privilege of organizing this joint meeting and of serving as the managers of our respective research programs. In carrying out these tasks, we learn from the achievements, and share the excitement, of the research of the many sponsored scientists and students whose names appear on the papers in the following pages. We also hope that this meeting will enhance your research efforts and will nurture future collaborations and initiatives.

We thank all of the researchers whose dedication and innovation have advanced our research and made this meeting possible and, we hope, productive. We hope that all of you will build on your successes and that we will assemble in a very few years for our next joint meeting.

We thank Karen Talamini of the Chemical Sciences, Geosciences and Biosciences Division, and Sophia Kitts and Rachel Smith of the Oak Ridge Institute for Science and Education for assisting in the technical and logistical aspects of this meeting.

John C. Miller

Lester R. Morss

Norman Edelstein

Heavy Element Chemistry and Separations
Contractors' Meeting Program

Sunday, April 27, 2003; 1800 - 2000 Registration, Cash Bar Reception, and Poster Setup

Monday Morning, April 28, 2003

700 - 800 Continental Breakfast at the hotel, provided by DOE. Poster Setup

800 Start of meeting - Introductory Remarks and Plenary Lecture I

800	Morss, Lester		Welcome and Introductions	Department of Energy, Office of Science, Chemical Sciences, Geosciences and Biosciences Division, SC-14
810	Miller, John C.		Welcome and Introductions	Department of Energy, Office of Science, Chemical Sciences, Geosciences and Biosciences Division, SC-14
820 - 900	Sattelberger, A.	PL-1	Heavy Element Chemistry in the 21st Century: Challenges and Opportunities	Chemistry Division, Los Alamos National Laboratory, Los Alamos

905 Short presentations - Oral session I

905	Yeung, Edward S.	P1-1	Single Molecule Studies of Chromatographic Events	Ames Laboratory, Iowa State University
915	Lukens, Wayne	P1-2	X-ray Absorption Fine Structure Studies of Organoactinide Complexes	Actinide Chemistry Group, Lawrence Berkeley National Laboratory
925	Assefa, Z.	P1-3	Intra-molecular energy transfer studies from oxo- and nitrogen ligating hetero-cyclic ligands to actinide ions	Oak Ridge National Laboratory
935	Pronko, Peter P.	P1-4	Isotopically Enriched Films and Nanostructures by Ultrafast Pulsed Laser Deposition	Center for Ultrafast Optical Science (CUOS), University of Michigan
945	Heaven, Michael C.	P1-5	Spectroscopic Studies of Prototype Actinide Compounds	Department of Chemistry, Emory University
955	Maciel, Gary E.	P1-6	Multinuclear Magnetic Resonance Study of Silica and Modified Silicas	Department of Chemistry, Colorado State University, Fort Collins

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1005	Liu, Guokui	P1-7	Electronic Properties of Heavy Elements in Condensed Phases	Chemistry Division, Argonne National Laboratory
1015	Harris, Joel M.	P1-8	Spectroscopic Methods to Characterize Interfacial Electric Fields and Metal-Ion Binding to Immobilized Ligands	Department of Chemistry, University of Utah
1025	Dorhout, Peter K.	P1-9	Synthesis of New Actinide Main-Group Metal Materials: Structures and XANES Spectroscopic Studies of Plutonium Polyselenides	Department of Chemistry, Colorado State University

1035 - 1125 Coffee break and Poster Session I

1125 Short presentations - Oral session II

1125	Gregorich, Kenneth E., Nitsche, Heino, and Hoffman, Darleane C.	P2-1	Chemistry of Elements 108 and 112	Nuclear Science Division, Lawrence Berkeley National Laboratory
1135	Wilkerson, Marianne P.	P2-2	The First Observation of 5f-5f Luminescence from a Transuranic Actinyl Complex	Chemistry Division-Advanced Diagnostics and Instrumentation, Los Alamos National Laboratory
1145	Pemberton, Jeanne E.	P2-3	Raman Spectroscopy of Chromatographic Stationary Phases: Towards a Molecular Description of Retention	Department of Chemistry, University of Arizona
1155	Chiarizia, R., Beitz, J. V., Nash,	P2-4	Heavy Element Aggregation Phenomena	Chemistry Division, Argonne National Laboratory
1205	Grey, Clare P.	P2-5	NMR Studies of Structure and Gas Binding in Molecular Sieves	Chemistry Department, SUNY Stony Brook
1215	Nitsche, Heino, Gregorich, Kenneth E., and Hoffman, Darleane C.	P2-6	The Chemistry of Rutherfordium and Dubnium (Elements 104 and 105)	Nuclear Science Division, Lawrence Berkeley National Laboratory

1225	Sepaniak, Michael J.	P2-7	Advancing the Capabilities of Surfaced Enhanced Raman Scattering in Chemical Analysis	Department of Chemistry, University of Tennessee, Knoxville
	Laue, Carola A	P2-8	Creating Isotopes of Elements 114, 116, and 118 — The Essential First Step to Their Chemical Characterization	Analytical and Nuclear Chemistry Division, Lawrence Livermore National Laboratory

1235 Lunch - Provided by DOE

1310 - 1410 Poster Session II

1410 Short presentations - Oral session III

1410	Fulton, John L.	P3-1	Details of Ion Hydration and Ion-Pair Structure from X-ray Absorption Spectroscopy and Molecular Dynamics Simulations	Fundamental Sciences Division, Pacific Northwest National Laboratory
1420	Clark, Sue B. and Ewing, Rodney C.	P3-2	Actinide Incorporation and Radiation Effects in U(VI) Solids	Department of Chemistry and Center for Multiphase Environmental Research, Washington State University; Department of Nuclear Engineering and Radiological Sciences, University of Michigan
1430	Lindle, Dennis W. and Shuh, David K.	P3-3	Molecular Environmental Science Using Synchrotron Radiation: Chemistry and Physics of Waste Form Materials	Department of Chemistry, University of Nevada, Las Vegas, and Chemical Sciences Division, LBNL
1440	Soderholm, L. and Jensen, Mark	P3-4	The Actinide Facility	Chemistry Division, Argonne National Laboratory
1450	Cheetham, Anthony	P3-5	Sorption, Catalytic and Ion-Exchange Properties of Nanoporous Nickel Phosphates	Materials Research Laboratory, University of California, Santa Barbara
1500	Felker, L. K.	P3-6	Advanced Fuel Cycle Initiative Support at the Radiochemical Engineering Development Center	Nuclear Science and Technology Division, Oak Ridge National Laboratory

1510	Conradson, Steven	P3-11	Heterogeneity and Collective Phenomena in Crystalline Solids	Materials Science and Technology Division, Nuclear Materials and Technology Division, Chemistry Division
1520	Booth, Corwin H.	P3-12	Hybridization, delocalization, and disorder effects in *f*-electron intermetallics	Glenn T. Seaborg Center, Chemical Sciences Division, Lawrence Berkeley National Laboratory
1530	Haire, R. G.	P3-13	Pressure-induced Changes in Actinides: Importance for Understanding Actinide Bonding	Chemical Sciences Division, ORNL
	Alexander, C.W.	P3-7	Recovery of Long-Lived Fission Products from Highly-Irradiated Pu Targets	Nuclear Science and Technology Division, Oak Ridge National Laboratory
	Alexander, C.W.	P3-8	The Savannah River MK 18A Target Assemblies: A National Resource of Pu and Cm	Nuclear Science and Technology Division, Oak Ridge National Laboratory
	Martin, Rodger C.	P3-9	Neutron Sources for Cancer Therapy and Other Research at the Californium User Facility for Neutron Science	Nuclear Science and Technology Division, Oak Ridge National Laboratory
	Wham, R. M.	P3-10	Plutonium-238 Production Support Studies	Nuclear Science and Technology Division, Oak Ridge National Laboratory

1540 - 1630 Coffee break and Poster Session III

1630 Short presentations - Oral session IV

1630	Shuh, David K.	P4-1	Soft X-ray Synchrotron Radiation Investigations of Actinides and the Advanced Light Source Molecular Environmental Science Beamline	Actinide Chemistry Group, Chemical Sciences Division, The Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory
1640	Miller, J.D.	P4-2	Micellar Surface Structures	Metallurgical Engineering, University of Utah

1650	Hay, Benjamin P.	P4-3	Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modeling and Host Design	Chemical Sciences Division, Pacific Northwest National Laboratory
1700	Basaran, Osman	P4-4	Fundamentals Of Electric Field-Enhanced Multiphase Separations And Analysis	School of Chemical Engineering, Purdue University
1710	Guiochon, Georges	P4-5	Study of the Homogeneity of Adsorbent Surfaces	Department of Chemistry, The University of Tennessee, Knoxville
1720	Wirth, Mary J.	P4-6	Separations and Analysis of Proteins Using Living Polymer Chains on Surfaces	Department of Chemistry & Biochemistry, University of Delaware
1730	Belfort, Georges	P4-7	Chemical interactions between protein molecules and polymer materials: Surface chemistry affects adhesion and protein conformational changes in the bioprocessing environment	Howard Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute
1740	Muralidharan, Subra	P4-8	Metal Ion Recognition Through Organized Microstructures	Department of Chemistry and the Nanotechnology Research and Computation Center, Western Michigan University, Kalamazoo
1750	Raymond, Kenneth N., Xu, Jide	P4-9	Exploring Lanthanide and Actinide Supramolecular Chemistry	Actinide Research Group, Chemical Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemistry, University of California, Berkeley
1800	Moyer, Bruce A.	P4-10	Principles of Chemical Recognition and Transport in Extractive Separations: Anion Recognition in Salt Extraction by Ion Receptors	Chemical Sciences Division, Oak Ridge National Laboratory
1810	Blanchard, Gary J.	P4-11	Controlling Mass Transport Properties of Interfaces Using Ultrathin Polymer Layers	Department of Chemistry, Michigan State University

1820 - 2000 Poster Session IV - And Cash Bar

2000 Dinner on your own

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Contractors' Meeting Program

Tuesday Morning, April 29, 2003

700 - 800 Continental Breakfast at the hotel, provided by DOE. Poster Setup

800 Start of meeting - Plenary Lecture II

800 - 840	McCabe, Daniel	PL-2	Radiochemical Separations for Savannah River Site and Hanford Waste Treatment Plant High-Level Nuclear Waste Solutions	Westinghouse Savannah River Co., on detail to EM-54, Cloverleaf Bldg.

845 Short presentations - Oral session V

845	Bosnich, Brice	P5-1	Supramolecular Assembly and the Effects of Electrostatic Interactions	Department of Chemistry, University of Chicago
855	Burns, Carol J.	P5-2	Organometallic Actinide Chemistry	Chemistry Division, Los Alamos National Laboratory, Los Alamos
905	Delmau, Lætitia H. and Moyer, Bruce A.	P5-3	Principles of Chemical Recognition and Transport in Extractive Separations: Comparing the Performance Characteristics of Calix[4]arene Azacrown-6 with Calix[4]arene Oxacrown-6	Chemical Sciences Division, Oak Ridge National Laboratory
915	Paine, Robert T.	P5-4	Preorganized and Immobilized Ligands for Metal Ion Separations	Department of Chemistry, University of New Mexico
925	Clearfield, Abraham	P5-5	The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded to Layered Arrays	Department of Chemistry, Texas A&M University
935	Choppin, Gregory R.	P5-6	Research in Actinide Chemistry	Department of Chemistry and Biochemistry, Florida State University
945	Bartsch, Richard A.	P5-7	New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations	Texas Tech University
955	Albrecht-Schmitt, Thomas E.	P5-8	Understanding the Solid State Chemistry of Actinyl Compounds Containing Heavy Oxoanions	Department of Chemistry, Auburn University
1005	Alexandratos, Spiro D.	P5-9	Immobilized Ligand-Modified Scaffolds: Design, Synthesis and Ionic Recognition	Department of Chemistry, Hunter College of the City University of New York

1015	Freeman, Benny D.	P5-10	Nanostructured Hybrid Materials for Advanced Membrane Separations	Department of Chemical Engineering, The University of Texas at Austin

1025 - 1125 Coffee break and Poster Session V

1125 Short presentations - Oral session VI

1125	Runde, Wolfgang	P6-1	New Insight into the Coordination Chemistry of Plutonium and Americium: Synthesis and Structural Characterization of Pu(III) oxalates and Am(III) iodates	Chemistry Division, Los Alamos National Laboratory
1135	Bonnesen, Peter V.	P6-2	Principles of Chemical Recognition and Transport in Extractive Separations: Synthesis of Dibenzo-14-Crown-4 Ethers Bearing Fluoroalcohol Lariats	Chemical Separations Group, Chemical Sciences Division, Oak Ridge National Laboratory
1145	Sessler, Jonathan L. and Anslyn, Eric V.	P6-3	Separations and Heavy Element Chemistry in the Sessler Group	Department of Chemistry & Biochemistry, Institute for Cellular and Molecular Biology, The University of Texas at Austin
1155	Davis, Jeffery T.	P6-4	Self-Assembled Ionophores	Department of Chemistry and Biochemistry, University of Maryland, College Park
1205	Raymond, Kenneth N., Gordon, Anne	P6-5	Siderophore-Based Water Soluble Ligands for Actinide Decorporation	Actinide Research Group, Chemical Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemistry, University of California, Berkeley
1215	Rogers, Robin D.	P6-6	Fundamentals of Solute Partitioning in Aqueous Biphasic Systems	Center for Green Manufacturing, The University of Alabama, Tuscaloosa
1225	Morris, David E.	P6-8	Actinde Chemistry Under Alkaline Conditions	Materials Science and Technology Division, and Biosciences Division, Los Alamos National Laboratory

No poster	Bright, Frank V.	P-6-9	Studies of Solvation Processes in Supercritical Fluids and Room Temperature Ionic Liquids	Department of Chemistry, Natural Sciences Complex, University at Buffalo, The State University of New York
	Rogers, Robin D.	P6-7	Aqueous Biphasic Systems: Novel Delivery Systems and Novel Applications	Center for Green Manufacturing, The University of Alabama, Tuscaloosa

1240 Lunch, Provided by DOE

1320 - 1420 Poster Session VI

1420 Short presentations - Oral session VII

1420	Antonio, Mark R., Dietz, Mark L. and Jensen, Mark P.	P7-1	Probing Metal-Ligand Interactions through Actinide-Polyoxometalate Complexes and Room-Temperature Ionic Liquids	Chemistry Division, Argonne National Laboratory
1430	Tsouris, Costas	P7-2	Fundamental Studies in Novel Separations	Nuclear Science and Technology Division, Oak Ridge National Laboratory
1440	Neu, Mary P.	P7-3	Actinide(III, IV) Phosphine Oxide and Nitrile Complexes	C-SIC, Chemistry Division, LANL
1450	Yonker, Clement R.	P7-4	Reaction Chemistry in Supercritical Fluid Solutions	Fundamental Science Division, Pacific Northwest National Laboratory
1500	Rao, Linfeng	P7-5	Chemical Thermodynamics of Actinides in Solution Under Non-Conventional Conditions	Chemical Sciences Division, Lawrence Berkeley National Laboratory
1510	Bruening, Merlin	P7-6	Multilayered Polyelectrolyte Films as Highly Selective Nanofiltration Membranes	Department of Chemistry, Michigan State University
1520	Gibson, J. K.	P7-7	Gas-Phase Actinide Ion Chemistry: Thermochemistry of Actinide Oxide Molecules	Chemical Sciences Division, ORNL

1530	Dai, Sheng	P7-8	Hierarchical Synthesis of Materials for Separation	Chemical Sciences Division, Oak Ridge National Laboratory
1540	Andersen, Richard A.	P7-9	Synthetic and Structural Studies of Organoactinides and Other Compounds	Chemical Sciences Division, Lawrence Berkeley National Laboratory
No poster	Rauchfuss, Thomas B.	P7-10	Molecular Containers with Exquisite Ion Selectivity	School of Chemical Sciences, University of Illinois at Urbana-Champaign

1550 - 1640 Coffee break and Poster Session VII

1640 Short presentations - Oral session VIII

1640	Bursten, Bruce E.	P8-1	The Electronic Structure of Heavy Element Complexes	Department of Chemistry, The Ohio State University
1650	Bohn, Paul W.	P8-2	Molecular Aspects of Transport in Thin Films of Controlled Architecture	Department of Chemistry, University of Illinois at Urbana-Champaign
1700	Martin, Richard L. and Hay, P. Jeffrey	P8-3	Density Functional Studies of Organoactinide Complexes and Actinide Oxide Materials	Theoretical Division, Mail Stop B268, Los Alamos National Laboratory
1710	Hupp, Joseph T.	P8-4	New Supramolecular-Assembly-Derived Membranes Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities	Dept. of Chemistry and Dept. of Chemical Engineering, Northwestern University
1720	Pitzer, Russell M.	P8-6	Electronic Structure of Actinide Systems	Department of Chemistry, Ohio State University
1730	Koros, William J. and Paul, Donald R.	P8-7	Polymers with High Permeabilities & Selectivities for Gas & Vapor Separations	Department of Chem. Engr., Georgia Inst. of Tech. (Koros) & Univ of Texas, Austin (Paul)
1740	Scuseria, Gustavo E.	P8-8	Relativistic all-electron calculations including the spin-orbit interaction using hybrid density functionals	Department of Chemistry, Rice University
1750	Way, J. Douglas	P8-9	Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes	Dept. of Chemical Engineering, Colorado School of Mines

1800	Yaghi, Omar M.	P8-10	Design of Pore Size and Functionality in Metal-Organic Frameworks for Separation of Organics and Storage of Methane and Hydrogen	Department of Chemistry, University of Michigan, Ann Arbor
1810	Crooks, Richard M., Sun, Li	P8-11	Analytical Applications of Single-Pore Membranes Based on Carbon Nanotubes	Department of Chemistry, Texas A&M University
	Snurr, Randall Q., Hupp, Joseph T., Nguyen, SonBinh T.	P8-5	Molecular Modeling and Design of Novel Nanoporous Materials for Selective Membrane Separations and Energy Storage	Depts. of Chemical Engineering and Chemistry, Northwestern University

1830 - 2100 Dinner at the hotel

2100 - 2230 Poster Session VIII - And Cash Bar

Wednesday Morning, April 30, 2003

730 - 830 Continental Breakfast at the hotel, Provided by DOE

830-1000 Summary Session

1000-1030 Coffee Break

1030-1200 Future Directions Session, Meeting End

Abstract P1-1

Single Molecule Studies of Chromatographic Events

Edward S. Yeung; Principal Investigator
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Hungwing Li, student
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Overall research goals: The study of single-molecule adsorption, desorption and motion at a liquid-solid interface can provide insights into molecular dynamics, biosensor design, novel materials and basic separation theory. It is well known that both electrostatic and hydrophobic interactions govern adsorption at liquid-solid interfaces. These fundamental interactions are the foundation for many chromatographic separations. Both retention and band broadening in chromatography and electrophoresis have been explained by using statistical theory. Direct observation of individual molecular motion and interactions at the liquid-solid interface would add valuable details regarding these and other related phenomenon. Such insights can potentially lead to novel separation modes for a variety of species.

Specific objectives for 2002-2003: In one project, we have shown that individual adsorption/desorption events can be monitored in real time for single molecules. The next step is to relate this directly to bulk chromatographic observations. The ratio of adsorption time to desorption time is the capacity factor k' in chromatography. We will test this statistical concept on bare fused-silica and on C18 surfaces with various water/organic solvents by establishing direct correlations between the two types of experiments. Such correlations will have fundamental implications in the theory of chromatography. In a second project, we have been able to image single particles or bacteria during electrophoresis and have observed unusual motion and aggregation. We plan to systematically study this effect to elucidate the mechanisms involved. This type of insight should eventually allow the development of novel separation modes. In particular, separation of bacteria may lead to rapid identification needed to counter bioterrorism.

Significant Achievements: We report the unexpected radial migration of DNA molecules in capillary electrophoresis (CE) with applied Poiseuille flow. Such movement can contribute to anomalous migration times, peak dispersion and size and shape selectivity in CE. When Poiseuille flow is applied from the cathode to the anode, DNA molecules move toward the center of the capillary, forming a narrow, highly concentrated zone. Conversely, when the flow is applied from the anode to the cathode, DNA molecules move toward the walls, leaving a DNA-depleted zone around the axis. We showed that the deformation and orientation of DNA molecules under Poiseuille flow was responsible for the radial migration. By analyzing the forces acting on the deformed and oriented DNA molecules, we derived an expression for the radial lift force, which explained our results very well under different conditions with Poiseuille flow only, electrophoresis only, and the combination of Poiseuille flow and electrophoresis. Factors governing the direction and velocity of radial migration were elucidated. Potential applications of this phenomenon include an alternative to sheath flow in flow cytometry, improving precision and reliability of single molecule detection, reduction of wall adsorption, as well as size separation with a mechanism akin to field-flow fractionation. On the negative side, non-uniform electroosmotic flow (EOF) along the capillary or microfluidic channel is common in CE, and radial migration of certain analytes cannot be neglected.

Publications, 2002-2003:

"One-Step Concentration of Analytes Based on Dynamic Change in pH in Capillary Zone Electrophoresis", W. Wei, G. Xue, and E. S. Yeung, Anal. Chem., 74, 934 (2002).
"Combinatorial Study of Zeolites in Catalyzing the Acylation of Benzene via Laser-induced Fluorescence Imaging", H. Su and E. S. Yeung, Appl. Spectrosc., 56, 1044 (2002).
"Laser-induced Fluorescence Detection in High-throughput Screening of Heterogeneous Catalysts", H. Su and E. S. Yeung, in High Throughput Analysis: A Tool for Combinatorial Materials Science, Plenum, New York, in press (2003).
"Selective Genotyping of Individual Cells by Capillary Polymerase Chain Reaction", H. Li and E. S. Yeung, Electrophoresis, 23, 3372 (2002).
"Combinatorial Enantiomeric Separation of Diverse Compounds using Capillary Array Electrophoresis", W. Zhong and E. S. Yeung, Electrophoresis, 23, 2996 (2002).
"On-line Concentration of Proteins and Peptides in Capillary Zone Electrophoresis with an Etched Porous Joint", W. Wei and E. S. Yeung, Anal. Chem., 74, 3899 (2002).
"Anomalous Radial Migration of Single DNA Molecules in Capillary Electrophoresis", J. Zheng and E. S. Yeung, Anal. Chem., 74, 4536 (2002).
"Electrophoretic Quantitation of Nucleic Acids without Amplification by Single-Molecule Imaging", T. Anazawa, H. Matsunaga, and E. S. Yeung, Anal. Chem., 74, 5033 (2002).
"Chemical Imaging of Surface Reactions by Multiplexed Capillary Electrophoresis", M. Christodoulou and E. S. Yeung, Anal. Chem., 74, 5414 (2002).
"Single-Molecule Optical Imaging", E. S. Yeung, in McGraw-Hill Yearbook of Science and Technology, McGraw-Hill: New York, 392 (2003).
"Mechanistic Aspects in the Generation of Apparent Ultra-High Efficiencies for Colloidal (Microbial) Electrokinetic Separations", D. W. Armstrong, M. Girod, L. He, M. A. Rodriguez, W. Wei, J. Zheng, and E. S. Yeung, Anal. Chem., 74, 5523 (2002).
"Dynamics of Single Protein Molecules at a Liquid/Solid Interface: Implications in Capillary Electrophoresis and Chromatography", S. H. Kang and E. S. Yeung, Anal. Chem., 74, 6334 (2002).
"Mechanism of Microbial Aggregation during Capillary Electrophoresis", J. Zheng and E. S. Yeung, Anal. Chem., 75, 818 (2003).
"Counting Single DNA Molecules in a Capillary with Radial Focusing", J. Zheng and E. S. Yeung, Aust. J. Chem., 56, 1 (2003).
"By the Numbers", E. S. Yeung, SPIE OE Magazine, February 2003, p.24.

Abstract P1-2

X-ray Absorption Fine Structure Studies of Organoactinide Complexes

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Collaborators:
Prof. Christopher Cummins and Paula Diaconescu (graduate student): Massachusetts Institute of Technology.
Dr. Jacqueline Kiplinger: Los Alamos National Laboratory
Prof. Richard Andersen: Lawrence Berkeley National Laboratory

Overall research goals: The main purpose is to better understand bonding and structure in organoactinide complexes using x-ray absorption fine structure spectroscopy (XAFS). The main goal is to investigate complexes with ambiguous formal oxidation states or metal-ligand multiple bonding.

Specific objectives for 2002-2003: The main objective for this period is examining the XAFS spectra of uranium inverted sandwich complexes to understand the bonding in these complexes and to evaluate the effect of structural changes on the electronic structure of these complexes.

Significant achievements: The XAFS spectrum of the parent organouranium inverted sandwich complex,[1] $(\mu\text{-}C_7H_8)[U(N[Ad]Ar)_2]_2$ where Ad = 1-adamantyl, and Ar = 3,5-$Me_2C_6H_3$, was obtained. The results showed that the electron density around the uranium center was similar to that of U(III) complexes.[2]

Plans for future research on this project: Examine the XAFS spectra of a variety of organouranium complexes with metal-ligand multiple bonds to evaluate the effect of bond-order on the shift of the uranium L_3 absorption edge.

References:

(1) Diaconescu, P. L.; Arnold, P. L.; Baker, T. A.; Mindiola, D. J.; Cummins, C. C. *J. Amer. Chem. Soc.* **2000**, *122*, 6108.

(2) Diaconescu, P. L.; Lukens, W. W.; Cummins, C. C. *Orgaonometallics* **2003**, submitted.

Other publications from this project in 2002-2003:

Chabanas, M.; Baudouin, A.; Coperet, C.; Basset, J.-M.; Lukens, W.; Lesage, A.; Hediger, S.; Emsley, L. *J. Amer. Chem. Soc.* **2003**, *125*, 492.

Abstract P1-3

Intra-molecular energy transfer studies from oxo- and nitrogen ligating hetero-cyclic ligands to actinide ions

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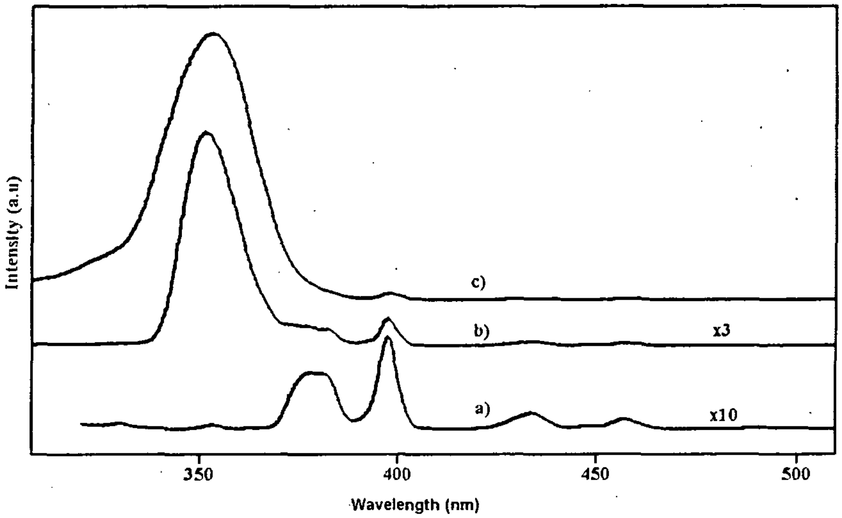
T. Yaita, Visiting Scientist
Dept. of Materials Science, Japan Atomic Energy Research Institute, Tokai, Japan.

We have embarked on studies of ligands possessing aromatic and/or hetero-aromatic groups that are easily excited by near UV-radiation, and hence are capable of enhancing excited-state, energy-transfers in donor/acceptor systems. Highly luminescent lanthanide complexes of cryptands, □-diketones, and several other macrocyclic ligands have been studied extensively over the years, although attention to the corresponding actinide species has been minimal. Such enhancements are particularly important in actinide research, as the hazards associated with these materials necessitate efficient and selective luminescent probes with ultraviolet and visible sensitizers.

We are currently assessing several ligands for intra-molecular energy-transfer processes with transuranium species. To the best of our knowledge, studies involving "sensitized" emissions in transuranium complexes have been limited to the □-diketonate systems, where oxygen linkages are encountered. In this presentation we report the first example of efficient energy-transfer from a nitrogen-coordinating ligand to a transuranium ion. Complexation of curium with a derivative of benzimidazole ligand (Biz) provided luminescence enhancement of several order magnitudes. The luminescence enhancement is obtained due to intra-molecular energy-transfer (ET) from the triplet (3□ □*) excited state of the ligand to the Cm(III) ion. Similar enhancements have also been obtained in Am^{3+} ions.



Excitation spectra in MeOH solutions: a) $CmCl_3$; b) Biz :Cm^{3+} (1:1);
c) Biz:Cm^{3+} (2:1). The concentration of Cm^{3+} is 5 mmol in all samples. Mole ratios given in parenthesis correspond to initial concentrations; pH was adjusted to 1 with HCl.

The excitation spectrum shown for a 5 mmol $CmCl_3$ solution in MeOH (spectrum "a") was obtained while monitoring the emitted light at 599.5 nm. The strongest bands corresponding to the $^8S_{7/2} \rightarrow {}^6I_{11/2}$, $^6P_{13/2}$ f- f transitions are observed at 397 and 378 nm, respectively. In "b" and "c", the 1:1 and 2:1 Biz:Cm^{3+} complexes show dramatic changes in their excitation spectra. A band at 351 nm now appears dominant, although direct f - f excitations (as shown in "a") are negligible in this spectral region. Hence, the excitation band at 351 nm corresponds to the ligand centered □□* transition.

Insight into the nature of the species formed in solution has been gleaned by studying the dependence of the spectral profile on ligand concentration. The addition of Biz to a 5 mmol $CmCl_3$ solution was found to red-shift the emission maximum (602 vs 599.2 nm) and increase the intensity dramatically. The sensitized emission intensity increases by a factor of ~3, 4, and 6 for a Biz:Cm^{3+} initial ratios of 2:1, 3:1, and 4:1, respectively. These changes, together with the in-growth of a shoulder at 605 nm with ligand concentration, are indicative of stepwise complexation at the metal center. The peaks at 602 and 605 nm are assigned to the 1:1 and 1:2 (M:Biz) adducts, respectively.

The Raman experiments also lend support for strong coordination between the Biz ligand and the actinide ion. The vibrational band for Biz at 1003 cm^{-1} (assigned to the breathing mode of the heterocyclic ligand) is shifted to 1023 cm^{-1}. A shift to higher wave numbers is indicative of strong coordination of the ligand to the Cm^{3+} center. In the 1350-1700 cm^{-1} region, which covers in-plane $\nu_{C=C}$ and $\nu_{C=N}$ stretching modes, the Raman signals are stronger after complexation, and split into several components. The band at 1590 cm^{-1} splits into bands at 1597, 1572 and 1543 cm^{-1} after complexation, indicative of a lowering in symmetry due to coordination of the ligand to the metal center.

Other oxo and nitrogen ligating heterocyclic ligands currently under consideration include dimethyl-diphenylpyridine dicarboxylamide, and dimethyl-diphenyl diglycolamide. As the fundamentals of sensitized luminescence are largely unexplored in the transuranium systems, an important opportunity exists to explore this area of spectroscopy as related to actinide chemistry.

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[***Sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, BES, US Dept. of Energy, under contract DE-AC05-00OR22725 with ORNL, managed & operated by UT-Battelle, LLC,***
]

"Isotopically Enriched Films and Nanostructures by Ultrafast Pulsed Laser Deposition"

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Overall Research Goals: This project is directed at developing, understanding and applying the phenomena of spontaneous isotopic separation and enrichment of elemental light isotopes around the central axis of ultrafast laser ablation plasmas [1]. A model is proposed and tested, whereby the spontaneous magnetic fields, both toroidal and longitudinal, which are known to exist in such femtosecond laser plasmas, act to confine the emitted ionic component of the plume and to induce centrifuge like rotation producing the observed enrichments.

Specific Objectives for 2002-2003

Our early work at 780 nm, 120 fs, 2 x 10^{14} W/cm^2 demonstrated the generality of the phenomena for isotopic elements in the periodic table up to mass 73. Research under this program has demonstrated similar separation effects for chemical species of ablated binary compounds such as the Ni/Cu alloy at 5 x 10^{15} W/cm^2. Comparison of these results with those obtained by conventional plasma centrifuges provides alluring similarities and reinforces the proposed model. Specific objectives for 2002-2003 are to find methods to increase the ionic yield of the femtosecond ablation process and to enhance the isotopic enrichment phenomena to increase its potential for practical applications.

Significant Achievements: Recent experiments, in the 10^{16} W/cm^2 range, have been directed at developing methods to enhance the ionic component of the plume, which normally also contains a large neutral fraction. The neutral fraction may or may not contain the enrichment, depending on the point in the expansion process where it achieved the neutral state. Experiments have been performed whereby the initial ablation plasma, while still in the one-dimensional expansion state, is subjected to a second time-delayed laser pulse. These time delays have been studied over the temporal range of 0.25 to 40 picoseconds. The mean plasma expansion distance for this time scale ranges from a small fraction of a micron to about 8 microns, well within the one-dimensional expansion region (typically taken to be on the order of the beam spot radius). It is found that the second pulse (with equal intensity to the first) produces a maximum 60% increase in the observed total ionic fraction of a silicon plume for a time delay on the order of 10 picoseconds. By comparing this effect using S and P polarized light it is determined that the second pulse affects the plasma through a predominantly resonance absorption process, the maximum of which is theoretically predicted to occur at 10 ps. This is confirmed by extracting the purely resonance portion of ionic yield and comparing it to theory. In addition to the increase in ionic yield at the optimum time delay, a study has been made of the isotopic enrichment of boron, from boron nitride, with and without the second pulse. It is observed in Fig. 1 that the second pulse affects the isotopic enrichment in a similar fashion as the ionic yield, producing a weighted average of 26% increase in central axis light isotope enrichment for the observed charge states of +1 to +3. For the specific charge state +2 the isotopic enrichment is seen to approach 60%.

Abstract P1-4

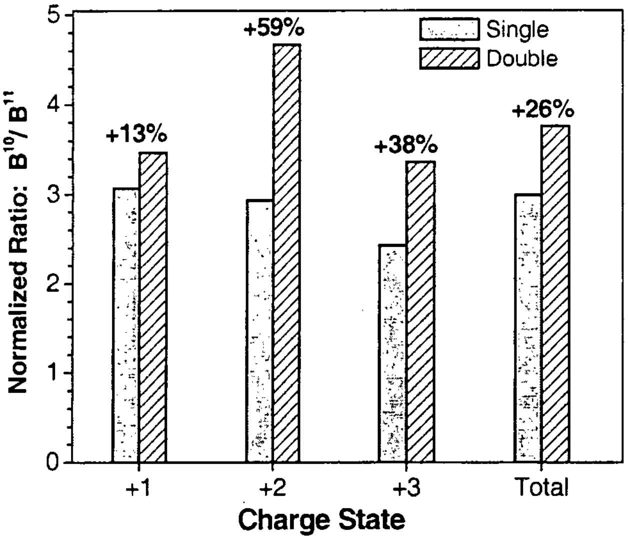

Fig.1: $^{10}B/^{11}B$ ratios on the central axis of the ablation plume as function of charge state, for double pulse with 10 ps time delay. The single pulse had a fluence of 2.2 KJ/cm2 and each double pulse half that value.

Plans for Future Research on this Project: Experiments are under way to investigate multi-pulse enhancements, where third, fourth, and higher numbers of pulses are used. Fundamental studies will be carried out on better understanding a femto-jet nozzle phenomena observed to affect the formation of nano-clusters in the ablation plume. Experiments are being conducted using a time resolved Langmuir probe to study the plasma temperature in the free expansion zone as a function of laser pulse intensity for single and multi-pulses. These results will be correlated with cluster size and density distributions. Attempts will be made to demonstrate isotopically and chemically enriched cluster formation as a follow on to these materials fabrication experiments.

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1). "Multi-diagnostic comparison of femtosecond and nanosecond pulsed laser plasmas", Z. Zhang, P.A. VanRompay, J.A. Nees, and P.P. Pronko, J. Appl. Phys. **92**, 2867 (2002).

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Spectroscopic Studies of Prototype Actinide Compounds

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Overall research goals:

High-level theoretical models of the electronic structures and properties of actinide compounds are being developed by several research groups. This is a challenging problem due to the need for explicit treatment of relativistic effects, and the circumstance that many of these molecules exist in states where the *f* and/or *d* orbitals are partially filled. Theoretical models must be tested and evaluated through comparisons with experimental results. Gas phase data are most suitable for this purpose. Unfortunately there have been very few gas phase studies of actinide compounds. We are filling that gap by carrying out gas phase spectroscopic studies of simple uranium and thorium compounds (oxides and halides). Multiple resonance and jet cooling techniques are being used to unravel the very complex electronic spectra of these compounds. We are also investigating the potential for using empirically adjusted Ligand Field Theory (LFT) models to interpret and predict the electronic energy level patterns.

Specific objectives for 2002-2003:

(i) Characterize the more intense electronic transitions of UO_2 in the visible and near UV spectra range. (ii) Obtain rotationally resolved spectra for bands of UO_2 that originate from the ground state. (iii) Develop a LFT model of the low-lying electronic states of UO_2. (iv) Use two-color threshold ionization techniques to obtain accurate ionization potentials for UO and UO_2. (iv) Develop the capability for recording mass analyzed threshold ionization (MATI) and zero kinetic energy (ZEKE) photoelectron spectra for UO and UO_2 (these techniques permit spectroscopic characterization of cations).

Significant Achievements:

Gas phase samples of UO and UO_2 were generated by pulsed laser vaporization of a uranium target. The ablated plume was entrained in a flow of He that contained 0.1% O_2 to facilitate oxide formation. The resulting gas mixture was cooled by supersonic expansion, and the core of the expanding gas was transmitted to a time-of-flight mass spectrometer. The metal oxides were photo-ionized by 10 ns laser pulses. Two-photon sequential ionization via resonant intermediate states was used to record excitation spectra and determine ionization thresholds.

The electronic spectrum of UO was previously investigated in our laboratory using laser induced fluorescence[1,2]. In the present study the ionization potential of UO was measured by tuning the first laser to the Q-branch feature of the [17.613]5-X(1)4 transition at 17613.97 cm^{-1}. A sharp ionization threshold was located when the second laser was tuned to 30823 cm^{-1}. Taking the local field of the mass spectrometer into account, (92 cm^{-1} shift) this yields an ionization potential of 6.017±0.004 eV. This result is far from the currently accepted experimental value of 5.6±0.1 eV[3,4]. Despite the use of supersonic cooling, single photon ionization measurements showed that UO trapped in metastable electronically excited states was present in the beam. It is likely that thermally populated excited states were responsible for the low ionization potentials obtained in the previous investigations.

Electronic spectra for gas phase UO_2 had not been reported previously. Consequently, we began our investigation of this molecule by searching for band systems in the visible and near UV spectral range. This search was guided by the *ab initio* calculations of Chang and Pitzer[5], who predicted strong transitions from the $X^3\Phi_{2u}$ ground state derived from the (*5f7s*) configuration that fall in the 526 – 490 nm range. Excitation spectra recorded in this range revealed the group of four bands shown in Fig. 1. The successive bands were separated by approximately 50 cm^{-1} intervals. A similar structure was observed in the 551-554 nm range, with the strongest and most blue-shifted feature at 551 nm (18149 cm^{-1}).

Threshold ionization measurements that utilized the bands shown in Fig. 1 demonstrated that they are members of a Δv=0 vibrational sequence. The intervals for the upper state, determined directly from the ionization threshold measurements, were close to 70 cm^{-1}. This information, combined with the first photon transition energies derived from Fig. 1, indicated that the lower state energy levels were separated by intervals of 120 cm^{-1}, consistent with the expected bending vibrational frequency. Based on the calculations of Chang and Pitzer[5] and our own Ligand Field Theory model, we assign the bands in Fig. 1 to the $(5f7p)^3\Pi_{2g}$-$(5f7s)X^3\Phi_{2u}$ transition. The band system near 552 nm is ascribed to the $(5f7p)^3\Gamma_{3g}$-$(5f7s)X^3\Phi_{2u}$ transition.

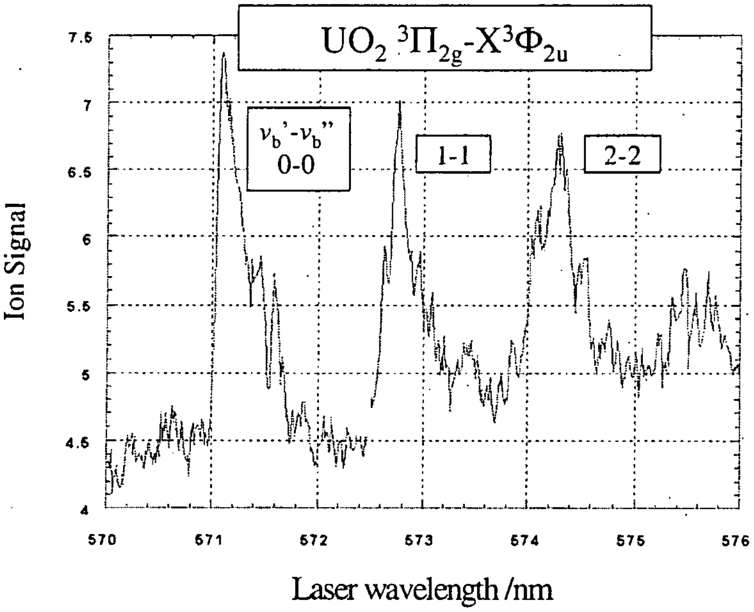

Figure 1. Excitation spectrum of UO_2

Band I in Fig. 1 originates from the ground state zero-point level. Consequently, ionization potential measurements were made with the first laser tuned to the maximum of this feature at 17614.0 cm^{-1}. The ionization threshold was located when the second photon was tuned through the range from 317 to 319 nm. Unexpectedly, we found that UO_2 exhibits delayed ionization at energies just above threshold. The UO_2^+ signal in the mass spectrometer decayed with a characteristic lifetime of approximately 100 ns. To our knowledge this is the first time that delayed ionization has been seen for a triatomic molecule. This phenomenon was used to advantage as the ionization threshold obtained by observing the delayed ions was sharper than that obtained by detecting the total ion current. The first ionization potential was at 6.09±0.01 eV, some 0.7 eV higher than the accepted value of 5.4±0.1 eV reported by Rauh and Ackerman[3] and Capone et al.[4] It is impressive to note that recent electronic structure calculations for UO_2 predict ionization energies that lie in the range of 6.0-6.3 eV[6,7]. Gagliardi et al.[6] speculated that the low ionization potentials obtained by experiment reflected the ionization of thermally excited states of UO_2. The present results strongly support that interpretation.

In searching for the ionization threshold of UO_2 we discovered a number of one-color resonances (ionization due to absorption of two UV photons). Several of these band systems exhibited the low frequency sequence structure illustrated by Fig. 1. The electronic assignments of these transitions have yet to be assigned.

Plans for future research:

We are configuring our system so that we can record MATI spectra for UO and UO_2. With this technique we should be able to resolve the vibrational structures of UO^+ and UO_2^+ in their electronic ground states. Low-lying electronic states of the ions should also be observable. Next we will switch to recording ZEKE spectra for UO and UO_2. The resolution of these measurements should be sufficient to expose the rotational structure of UO^+. Spectroscopic studies and IP measurements for ThO, ThO_2 and UF will be carried out. LFT models of these systems will be developed in parallel with the experimental efforts.

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Abstract P1-6

Multinuclear Magnetic Resonance Study of Silica and Modified Silicas

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Our recently renewed DOE project had focused primarily on the development and applications of solid-state NMR for examining the chemical and physical states of pollutants (e.g., trichloroethylene, acetone, benzene, thio-organophosphate ester pesticides) on soil and soil components (humic materials, silica, clays). In our recently begun grant period, emphasis has shifted to fundamental studies of one important segment of that broad scope, specifically a fundamental study of the detailed structure and reactivity of the silica surface.

Starting with the pioneering work of Dean Sindorf in his Ph.D. thesis project in the late 1970s, our research group has devoted much attention to the solid-state NMR study of silicas and modified silicas. Sindorf showed for the first time that $^1H \rightarrow X$ cross polarization (CP) (with, in this case, $X = {}^{29}Si$ in silica), in conjunction with magic-angle spinning (MAS), provides a surface-selective NMR technique for the study of high surface area materials. Sindorf's work demonstrated that, because the silicon atoms of terminal silanols (Q2, $Si(OH)_2$), single silanols (Q3, SiOH) and siloxane sites (Q4, >Si<) could be distinguished according to chemical shifts in $^1H \rightarrow {}^{29}Si$ CP-MAS experiments that favor surface site over interior sites, it became possible to employ NMR to study the transformations that occur at the silica surface in such processes as dehydration (and rehydration) and silylation. This and related studies in our group and other groups were followed in the mid-1980s by studies in our laboratory by Charles Bronnimann, who showed that the state of hydrogen bonding in silica silanols could be elucidated by the ^1H CRAMPS technique. Our 1978-1990 work indicated that geminal silanols were well modeled by a OH-terminated 100 plane of the beta-cristobalite crystal structure and account for most of the hydrogen-bonded silanols; similarly, the 111 beta-cristobalite surface modeled Q_3 silanols, accounting for most of the non-hydrogen-bonded silanols at a silica surface.

Research Associate I-Ssuer Chuang has, since the late 1980s, carried out a series of CP-based experiments designed to correlate the Si-coordination information provided by ^{29}Si NMR with the hydrogen bonding information provided by ^1H NMR. These experiments led to the conclusion, contrary to the earlier structural models, that *both* Q2 and Q3 silanols can be *either* hydrogen bonded or not hydrogen bonded and have inspired a new level of detail in modeling of the silica surface. These improved structural models rest on the concept of *intersections* of 100 and 111 planes and seem capable of accounting for the large volume of NMR and IR data that has been generated in several laboratories during the past 20 years, but have not been explicitly tested or evaluated *experimentally*. Our current emphasis is based on the use of sterically tailored probing agents (alcohols and amines) to assess the populations of the various types of surface features that have been postulated; the steric properties of individual alcohols or amines will determine which type(s) of silanols can undergo protium-deuterium exchange with chosen probe molecules (to be assessed via ^1H-^{29}Si CP and ^1H CRAMPS NMR). For example, the hydroxyl hydrogens of t-butyl alcohol, but not certain tris(2,3,4-trialkylphenyl) carbinols, will be able to access (participate in protium-deuterium exchange with) sterically hindered silanols sties near the concave intersection of two 111-surfaces. Analogous convex intersections will be probed by amines and/or alcohols with a "wrap-around" shape that permits access of a central NH or OH functionality to silanols only at the vertex of 111-111 intersection. By carrying out an extensive set of ^{1}H-^{2}H-exchange/NMR detection experiments with a set of properly chosen probe molecules, the populations of postulated surface features will be determined. This steric strategy is supported by an ongoing program of detailed steric modeling by both mechanical and computer (MM) approaches.

In a second aspect of this project, the reactivities and reaction mechanisms of silica for conversions of two general types will be examined: 1) silylation by reagents with one, two, or three leaving groups and 2) reaction with "simple" organometallic agents (MeLi, MeMgBr, Me_2Zn and Me_3Al). Attention will focus on determining the characteristics of formation, and subsequent transformation, of surface species involving Si-CH_3 and metal-CH_3 attachments. Reactivities will be studied for silica gel, fumed silica and mesoporous silica pretreated by evacuation over a range of temperatures. The results will be correlated closely with the results of surface-structural studies.

Specific objectives for 2003-2004 include 1) completion of the MM (and MD) modeling of suitable probe molecules, 2) choosing any probe molecules that must be synthesized, 3) preliminary experimental results with selected probe molecules and 4) complete study of the $AlMe_3$/silica system.

Publications from this project in 2002-2003

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2. Mark R. Seger and Gary E. Maciel, NMR Study of the Fate of Adsorbed Chlorpyrophos," *Envir. Sci. Technol.* submitted.

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Abstract P1-7

Electronic Properties of Heavy Elements in Condensed Phases

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Overall research goals: This project's aim is to provide a predictive understanding of the electronic interactions of lanthanides and actinides in solutions and solids. We seek experimental identification and theoretical interpretation of the influence of electronic interactions between f-ions and their environments on such properties as covalence, orbital hybridization, and excited-state dynamics.

Specific objectives for 2002-2003: We conduct experimental studies to assess the strengths of the standard crystal-field theory and to evaluate the effects of f-ion covalence and orbital hybridization in condensed phases. The influence of electronic interactions is a central focus of our efforts, as demonstrated by studies in ligand bonding [1] and high-valent actinides [2] in solution. Electron-phonon interactions and their impact on photo-dynamics are being investigated using spectroscopic methods and computational simulation. [3,4] Specifically, the 5f-6d electronic transitions and charge-transfer mechanisms are also under study. [5]

Significant achievements: The structural and electronic origins of the enhanced covalence in actinide(III)-ligand bonds were examined and the bonding contrasted to that of equivalent lanthanide(III) complexes[1]. No structural difference was found between the lanthanide and actinide complexes that could account for the differences in thermodynamic bond strengths. The difference could also not be correlated to the small differences in the occupancy of the outermost metal-centered electronic states of the complexes. In a related effort, we have determined, using high-energy X-ray scattering, the electron distribution on UO_2^{2+} in perchlorate solution.[6] For studies of electronic properties of actinides in high oxidation states, we have stabilized Pu(VII) and obtained the appropriate optical and x-ray spectroscopic data.

A theoretical framework has been established for analyzing uranyl charge-transfer vibronic transitions and multiphonon-vibronic coupling to the f-d electronic transitions.[5] Our analysis indicates both local ion-ligand vibrational modes and acoustic lattice phonon modes can be strongly coupled to the f-d transitions, but have different characteristics defined by Huang-Rhys coupling parameter and line-width parameter. We have conducted experiments and theoretical analyses of confined ion-phonon interaction of heave element ions in nanocrystals, in which the density of phonon states is discrete and low-frequency modes are cut off. It was shown that nonradiative relaxation of lanthanide ions in nano-phosphors becomes significantly different than that exhibited by bulk phosphors with the same structure.[3,4]

Plans for future research on this project: The primary future research includes systematic experimental studies of f-element covalent bonding and orbital hybridization effects. Theoretical modifications of the crystal-field theory will be made for modeling the electronic interactions related to hybridization and covalent bonding. We will continue to study electron-phonon interactions and their impact on actinide bonding and dynamic properties, and we plan to explore the electronic properties of actinides in nano phases to understand aggregation, nano-crystallization, and anomalous phase transitions, which were observed in recent experiments, but lack a fundamental understanding [7].

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Spectroscopic Methods to Characterize Interfacial Electric Fields and Metal-Ion Binding to Immobilized Ligands

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The goals of this research are development of surface-sensitive spectroscopies for investigating chemical structure and reactions at liquid/solid interfaces. These spectroscopic tools are leading to understanding and control of interfacial chemistry that impacts both analytical methods (chromatography, solid-phase extraction, and sensors) and environmental transport and remediation (metal-ion complexation to bound ligands, adsorption interactions at surfaces). We are developing *in situ* spectroscopies, Raman, infrared, and fluorescence, capable of detecting sub-monolayer coverages of molecules at liquid/solid interfaces. We are currently using these tools to study electric fields at modified surfaces and metal-ion complexation of immobilized ligands.

High-sensitivity SERS monitoring of derivatized metal films is being applied to studies of electrochemical perturbation of structure and binding at modified metal surfaces. We are developing *in situ* surface-enhanced Raman spectroscopy (SERS) to investigate the effects of applied potential at solid/liquid interfaces. We have utilized Stark tuning of a C N stretching frequency from a terminal nitrile group incorporated into a mixed self-assembled monolayer (SAM). Self-assembled monolayers composed of $HS(CH_2)_nCN$ diluted in $HS(CH_2)_{10}CH_3$, were assembled at highly-polished polycrystalline Ag surfaces. The stretching frequency of the pendant nitrile was used to probe the local electric field via the vibrational Stark effect, in which vibrational peak position shifts proportionally to changes in local electric field (i.e., applied potential). Results show that the peak position of the nitrile stretch exhibits potential dependence (or tuning rate) expected for the magnitude of electric field predicted to exist within an alkane chain SAM [1].

SERS-based spectroelectrochemistry was also used to investigate interfacial structural properties of mixed self-assembled monolayers (SAMs) as a function of their composition. Mixed-monolayers were formed from ethanolic solutions containing 12-mercaptododecanenitrile and n-hepanethiol. The intensities of Raman scattering from modes associated with the nitrile and methyl termini were used to determine the relative composition of the mixed-monolayers. Stark tuning rates of the nitrile probe molecule were used to investigate phase-segregation of the mixed thiols versus surface composition [2]. We have also measured potential-dependent SERS spectra of a pendent nitrile group to investigate the structure of the diffuse double-layer. Spectra were acquired from a series of monolayers composed of alkanethiols of varying chain length with a fixed-length mercaptododecanenitrile probe molecule. The trends in the data were consistent with Gouy-Chapman theory, in which Stark tuning rates, and the interfacial electric fields from which they originate, depend on both distance of the probe from the electrode surface and the ionic strength of the aqueous phase. For measurements at the highest ionic strengths, the double-layer extended further into solution than predicted by Guoy-Chapman theory, consistent with the finite size of hydrated ions. These results demonstrate that this spectroelectrochemical experiment can characterize diffuse double-layer structure on a sub-nanometer distance scale [3].

Raman spectroscopy is being applied in our lab to the investigation of the interfacial chemistry of silica-immobilized 8-hydroxyquinoline (8HQ) for binding of metal ions over a wide range of solution conditions. Raman spectra of the deprotonated, neutral, protonated, and copper-complexed forms of the ligand can be distinguished allowing proton-transfer and metal-ion binding reactions of the ligand to be investigated. The observed pH dependence of metal-ion binding was corrected for surface-potential using the Boltzmann Equation, and the resulting equilibrium constant for binding of Cu^{2+} was independent of concentration over a 100-fold range [4]. In order to understand the effects of surface-immobilization on these reactions, a water-soluble 8HQligand was synthesized, 5-(p-sulfophenylazo)-8-hydroxyquinoline (SPAHQ), where a sulfonic-acid group substitutes for siloxane on the immobilized ligand. We used multivariate spectroscopy to investigate the proton-transfer and stepwise metal-ion complex formation reactions of the SPAHQ ligand in solution [5].

In an experiment that combines these efforts, we have immobilized a thiol-derivative of 8-hydroxyquinoline to an electrode surface, and acquired SERS spectra in the absence and presence of several different metal ions in solution that can bind to the 8HQ ligand. The spectroscopic data show modulation of the hydrazone-to-azo tautomerism of the ligand being influenced by the binding of the metal ion, which was consistent with observations on silica surfaces. At low concentrations of metal ions, we have observed *reversible potential control* over metal-ion binding. A surprise in these results was that positive surface potentials favored binding of metal cations, which is opposite of the Poisson-Boltzmann influence on the activity of cations in the double layer. We have carried out electronic structure calculations to estimate the dipole moment of the two tautomers in order to understand the effect of electric field on ligand tautomerism. Our results indicate that a positive electric field at the surface favors the active (azo-quinoline) form of the ligand; the sensitivity to potential is greater than would be expected from the product of the E-field with the dipole moment. The potential modulation appears to be changing the structure of the ligand directly by charge transfer through conjugated bonds to the surface. So far, the theory and experiment are converging on this conclusion. This could represent an important discovery since it illustrates a variation of ligand reactivity toward metal-ion binding by a direct electronic control over its structure.

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Synthesis of New Actinide Main-Group Metal Materials: Structures and XANES Spectroscopic Studies of Plutonium Polyselenides.

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Overall Goals of the Project

The goals of this project are to prepare new plutonium and neptunium main-group metal solid state compounds and to explore their structures and physical properties in an effort to understand structure-property relationships in actinide solids.

Objectives for FY03

The objectives this year have been to explore a new family of plutonium ternary materials and their physical properties. Interpretation of XANES data suggests that plutonium chalcogenides have significantly different absorption edge energy than their lighter congeners.

Significant Achievements

The number of known ternary and even binary plutonium chalcogenides, excluding oxides, is small compared to transition metal and rare earth compounds. There are only eight plutonium chalcogenide crystal structures known; all are binaries. A series of two and three dimensional thorium compounds was synthesized by Ibers and co-workers with the formulas KTh_2Q_6 (Q = Se, Te), $CsTh_2Se_6$, $CuTh_2Te_6$, and $SrTh_2Se_5$. The ternary compounds, KTh_2Q_6 and $CsTh_2Se_6$, are interesting because they have intermediate length Q-Q bonds. It is almost certain that thorium is in the 4+ oxidation state. Experiments were undertaken to determine if it was possible to synthesize a similar compound containing plutonium;. both 3+ and 4+ would be reasonable plutonium oxidation states. Our recent work is the synthesis and structural characterization of a new ternary plutonium selenide compound, KPu_3Se_{8-x}. This compound is compared to both its parent structure, $PuSe_2$, and the related ternary compound, KTh_2Se_6.

XANES experiments were undertaken to gain information on the electron density around plutonium in KPu_3Se_{8-x} and binary plutonium chalcogenides. Figure 1 plots the second derivative of absorption versus energy. Due to the complexity of the theory needed to predict XANES spectra, the determination of oxidation states is largely empirical. To determine an atom's oxidation state it is important to have available a number of standards in which the target atom is in similar chemical environment compared to the sample being studied. Unfortunately, the number of plutonium compounds previously studied using XANES is small. The key result from this study is that the absorption edges of these heavy chalcogenide systems appear close to the value found for plutonium metal (within 1-2 eV) versus that for PuO_2. This implies that the electronic environment around plutonium is very similar to that found in the metal. This is significantly different from what is found for PuO_2, , the "industry standard". The value for the oxide is much closer to what is found for Pu^{4+} in aqueous solutions. Though the overall trend was not unexpected due to the presence of the much softer S, Se, and Te atoms compared to O, the magnitude of the effect, and the similarity to plutonium metal, is interesting and important.

Sample	Edge Position (eV)
Pu Metal	18056
$PuSe_2$	18057
KPu_3Se_8	18057
PuO_2	18061

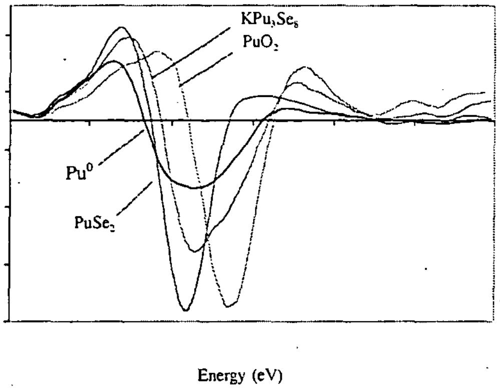

Figure 1. The plot of the second derivative of absorbance versus energy for the plutonium compounds examined in this study. The absorption edge is recorded where the second derivative first crosses the energy axis in the table on the left.

Future Plans and Potential Impact of These Studies

Plans for FY04 include evaluating the magnetic behavior of these compounds and preparing the Th, U and Np analogs for comparative studies. A recently installed Quantum Design MPMS 5 Tesla SQUID magnetometer in the plutonium facility (TA-55, PF-4 building) has enabled us to study Pu and Np samples in a hot-area laboratory. The unique electronic structure of the ternary phases may reveal important physical phenomena such as f-electron - conduction electron interactions. The impact of the current and future studies will be an improved understanding about the important structural, electronic and XANES behaviors of different neptunium and plutonium chalcogenides.

Publications from this project in press FY02-03

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Abstract P2-1

Chemistry of Element 108 and 112

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Overall research goals:

Determination of the chemical properties of the elements is the most fundamental goal in chemistry. Our world-leading studies of the chemical properties of the transactinide elements (Z=104-108) are unique within the US. Comparison of heavy element chemical properties with those of periodic table homologs and with theoretical predictions provides important insights for a better understanding of chemical properties throughout the periodic table and of yet unstudied elements.

Specific objectives for 2002-2003:

1) Produce and identify the element 112 isotope with mass 283 in the $^{48}Ca + ^{238}U \rightarrow ^{283}112 + 3n$ reaction. 2) Measure the chemical properties of $^{283}112$ to determine if it behaves like Hg (as expected by a classical periodic table extrapolation), or if it has a more noble gas character (as expected from some relativistic calculations). 3) develop methods, techniques and apparatus for the measurement of chemical properties of transactinide elements.

Significant achievements:

The first measurements of the chemical properties of element hassium (element 108, Hs) were made in collaborative experiments with the Paul Scherrer Institute (PSI, Switzerland) at the Gesellschaft für Schwerionenforschung (GSI, Germany). Hassium is a member of group 8 of the periodic table directly below Osmium. Osmium tetroxide easily formed in the presence of oxygen and is extremely volatile. In anticipation that hassium would have similar chemical properties, we developed the Cryogenic Thermochromatographic Separator (CTS) [KIR02] and tested it at the LBNL 88-Inch Cyclotron with osmium tetroxide. The CTS is a cryogenically-cooled thermochomatography column where the chromatography surfaces are Si P-I-N diodes. These P-I-N diodes also serve as detectors, allowing efficient detection of the radioactive decay of the Os or Hs atoms at the position (temperature) the tetroxide molecules are adsorbed. An improved version of the CTS, the Cryo On-Line Detector (COLD), was built at PSI and used in the Hs experiments at GSI. ^{269}Hs, with a half-life of near 10 seconds, was produced by the $^{26}Mg + ^{248}Cm \rightarrow ^{269}Hs + 5n$ reaction. The ^{269}Hs was stopped in a He/O_2 mixture, and immediately heated to 600°C to form the tetroxide. The $^{269}HsO_4$, together with the He/O_2 was passed through a narrow gap between two planes of P-I-N diodes, which were kept at negative temperature gradient. The positions along the P-I-N diode column of the alpha decay chains decay chains assigned to the decay of $^{268\text{-}269}Hs$ indicate an adsorption temperature for HsO_4 of -44°C. Comparison with OsO_4, adsorbing at -82°C, shows that HsO_4 is slightly less volatile than OsO_4 with adsorption enthalpies of -46 kJ/mol and -39 kJ/mol, respectively [DÜL02].

Recent claims from Dubna indicate that element 112 can be produced in the $^{48}Ca + {}^{238}U \rightarrow {}^{283}112 + 3n$ reaction with a cross section large enough for the production of a few atoms per week. The reported half-life for the $^{283}112$ spontaneous fission decay is ~5 minutes. If correct, the relatively large cross section and long half-life make $^{283}112$ an ideal candidate for studies of the chemical properties of element 112. We have undertaken a confirmation of the Dubna $^{283}112$ result with the Berkeley Gas-filled Separator (BGS) at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron [LOV02]. $^{283}112$ has not been observed at a cross section limit several times smaller than that reported at Dubna.

Element 112 should be directly below mercury in the periodic table. Amalgamation of Hg vapor on Au surfaces is a well-known and very specific chemical property, which may also be expected of element 112. On the other hand, relativistic calculations of the element 112 electronic structure show that the closed-shell $[Rn]5f^{14}6d^{10}7s^2$ configuration may be extremely inert, leading to noble gas behavior. Our PSI colleagues have built a modified version of the COLD detector, in which one row of the P-I-N detectors was replaced with a Au surface. This modified COLD is capable of detecting either Hg-like of Rn-like element 112. A collaborative experiment has been carried out during February and March 2003 at GSI to search for and determine the chemical properties of $^{283}112$. Preliminary results may be available at the time of the Contractors' meeting.

Plans for future research on this project:

Future plans for this transactinide chemistry project include: 1) Construction of the Berkeley Off-line Radioisotope Generator (BORG), a gas-jet transport device for fission products from spontaneous fission of a ^{252}Cf source. 2) Development of radiochemical separation techniques and apparatus for studies of the chemical properties of transactinide elements. 3) Relocation of the BGS and its use as a pre-separator for transactinide element chemical studies.

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Abstract P2-2

The First Observation of 5*f*-5*f* Luminescence from a Transuranic Actinyl Complex

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Overall research goals:

The interrelationships between molecular structures and spectroscopic signatures of actinide species are intriguing due to the innate complexity of the electronic behavior of this fascinating class of compounds. The density and strong spin-orbit coupling of states easily confound attempts to describe actinide species in terms of spatial parameters related to coordination environments. An insight into the nature of compounds with a single electron in the 5*f* shell could provide a unique opportunity to study the relationships between the 5*f* electronic properties and molecular structures in a discerning manner without introducing some of the typical complicating factors resulting from more than one electron in the valence shell. Furthermore, spectroscopic investigations of lower energy 5*f*-5*f* transitions perceptible in the near-infrared region may reveal a great amount of information because of the relatively low density of states and relaxation pathways. The long-term promise of this work is a practical means for beginning to develop a more systematic understanding of actinide electronic structures of more intricate but pervasive $5f^n$ (n>1) species containing coordination geometries and ligand sets accessed in common chemical environments, such as radiologically contaminated environmental wastes, actinide extraction media, and nuclear power plant streams.

The neptunyl ion ($Np(VI)O_2^{2+}$) is ideally suited to the goals of this spectroscopic investigation of $5f^1$ species for a variety of reasons. Many neptunium compounds in this +6 oxidation state are chemically stable (in comparison to those of uranium(V) and plutonium(VII)), and from a very practical standpoint, neptunium-237 is reasonably straightforward to handle in an appropriate radiological laboratory (unlike $^{231}Pa(IV)$). However, fundamental questions remain regarding the chemistry of neptunium (Np), such as its oxidation state and speciation as a function of chemical environment, its molecular coordination and bonding, and its chemistry at solid/solution interfaces. Studies of the early actinides, which lie in the critical region where 5*f* and 6*d* orbitals are being affected by the lanthanide contraction, have emphasized the chemical bonding of uranium, which is most stable as U(VI) and engages in more covalent bonding, and plutonium, which prefers lower oxidation states and is characterized by more ionic bonding.

Specific objectives for 2002-2003:

The overall goal of this project is to clarify the relationships between electronic structures and coordination environments of simple $5f^1$ actinide model systems by exploiting the breakthrough discovery that the neptunyl ion luminesces. Specific objectives in this experimental plan in 2002-2003 include: (1) synthesis of $Cs_2U(Np)O_2Cl_4$, and characterization of the matrix and analyte; (2) characterization of vibrational spectra using Raman and infrared absorption spectroscopies for comparison with emission spectra; (3) identification of pure electronic transition energies and vibronic structure, and measurement of excitation spectra; (4) determination of radiative lifetime behavior at room and low temperature; (5) measurement of luminescence quantum yields.

Significant achievements:

We have set up the appropriate instrumentation for collection of emission and excitation spectra, and measurement of radiative lifetimes. The instrumentation includes a tunable laser system using optical parametric processes to produce pulsed excitation spanning the visible and mid-infrared (450 to 2100 nm) and a state-of-the-art InP/InGaAs photomultiplier tube detector with an an extended spectral response from 0.3 to 1.7 µm, in conjunction with near-infrared array detection (0.8 to 1.7 µm) and accompanying computational and electronic interfacing. We have demonstrated that $Cs_2U(Np)O_2Cl_4$ luminesces with relatively high resolution and vibronic structure in the near-infrared at 77K, and more notably, it luminesces strongly at room temperature. Electronic and vibronic assignments for a portion of the spectrum are shown in Figure 1. The room temperature result is significant because it shows that the relaxation pathway from the assigned excited state is competitive with radiationless deactivation pathways to a large number of vibronic states accessible at room temperature. Radiative lifetimes of $Cs_2U(Np)O_2Cl_4$ are 60 µs at 77K and 19 µs at 32°C. These results imply that there are additional nonradiative pathways at room temperature.

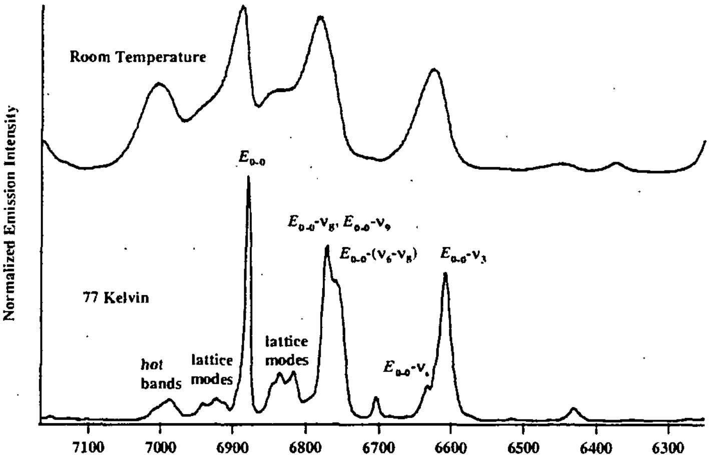

Figure 1. Luminescence spectra of $Cs_2U(Np)O_2Cl_4$ following excitation at 585 nm.

Plans for future research on this project:

We will complete excitation experiments of $Cs_2U(Np)O_2Cl_4$ using LMCT and higher energy 5*f*-5*f* transitions (13,000 to 20,100 cm^{-1}) of $NpO_2Cl_4^{2-}$. Comparisons of fluorescence excitation with absorption spectra may be useful in distinguishing higher lying 5*f* states from nearby LMCT states if decay pathways to the emitting low-lying 5*f* states have significantly different efficiencies. We are setting up appropriate instrumentation for determination of luminescence quantum yields of $Cs_2U(Np)O_2Cl_4$. In addition, we have identified another system for investigation of $5f^1$ electronic structure. The monooxo species $NpOCl_5^-$ might show interesting electronic structure because of the absence of a trans oxo ligand neatly eliminates the inversion center of the $D_{\infty h}$ neptunyl ion, thereby relaxing the parity selection rule.

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Abstract P2-3

RAMAN SPECTROSCOPY OF CHROMATOGRAPHIC STATIONARY PHASES: TOWARDS A MOLECULAR DESCRIPTION OF RETENTION.

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Raman spectroscopy is being used to gain insight into the molecular details of retention in two forms of chromatography: reversed-phase liquid chromatography (RPLC) and ion chromatography. Highlights of recent results are described below.

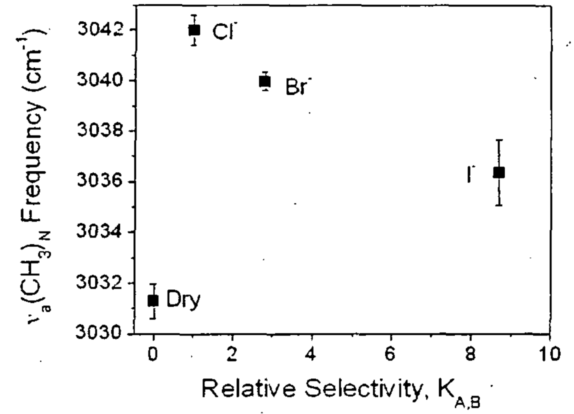
Raman Spectroscopy of Retention Mechanisms in RPLC. Despite several decades of intense effort, a fundamental understanding of the molecular basis of separation processes on alkylsilane-modified silicas used for RPLC has not been achieved. Of the numerous variables that affect retention processes, perhaps the least understood are the intermolecular interactions between chromatographic components such as solute-solvent, solute-stationary phase, solvent-stationary phase and intermolecular interactions within the stationary phase. Of equal importance are the effects that changes in chromatographic parameters (solvent, temperature, nature of the alkylsilane precursor, surface coverage and architecture) have on these interactions. Previous efforts in this laboratory have demonstrated that Raman spectroscopy is a powerful tool for investigating the fundamental intermolecular interactions that underlie retention in RPLC on alkylsilane-modified silicas. Many of the central advances in our understanding of such systems have resulted from the availability of a series of high-density octadecylsilane (C18) stationary phases on silica ranging in alkylsilane surface coverage from 3.1 μmol/m^2 to 6.5 μmol/m^2. (These stationary phases were synthesized and provided to us by our collaborator at NIST, Dr. Lane C. Sander.) The highest surface coverage essentially resembles a well-ordered self-assembled monolayer of C18 (the estimated maximum surface coverage of an alkylsilane on silica is based on the surface silanol density of ~8 μmol/m^2), and we have been able to understand changes in alkylsilane conformational order of the lower coverage phases in comparison to this maximum coverage system. We have also begun studies to ascertain whether a direct correlation exists between conformational order, as determined by Raman spectroscopy, and chromatographic behavior, as measured by the retention factor, k'. Preliminary evidence that very weak solute-stationary phase interactions can be observed comes from recent studies of small concentrations of toluene in methanol at stationary phase materials with coverages of 6.5 μmol/m^2 and 3.1 μmol/m^2. It was observed that small concentrations of toluene (5-25 mM) in methanol actually *increase the order* of the stationary phase by up to 0.5 units in the $I[\square_a(CH_2)]/I[\square_s(CH_2)]$ spectral indicator (out of a total range of 0.6 units) compared to neat toluene and up to 0.2 units in this indicator compared to neat methanol for *both* stationary phase coverages. These observations are a clear indication of the unique response of the stationary phase/solute/mobile phase organization to the sum total of intermolecular interactions occurring in the interface. Thus, in the case of a toluene solute in a pure methanol mobile phase, even though the interactions of the toluene solute with the stationary phase are sufficiently weak so as to preclude any retention, our spectral signatures of order are sensitive to these very weak interactions nonetheless. Moreover, the value of the $I[\square_a(CH_2)]/I[\square_s(CH_2)]$ spectral indicator in a mixed methanol:H_2O mobile phase has been shown to be a function of mobile phase composition (% H_2O) *and systematically varies with the retention factor of toluene.* The chromatographic data show, as expected, the increased retention of toluene on a C18 stationary phase as the H_2O content of a methanol:H_2O mobile phase is increased. Table 1 shows that the value of $I[\square_a(CH_2)]/I[\square_s(CH_2)]$ systematically decreases as the mobile phase H_2O content increases and the chromatographic retention factor, k', increases. Although the relationship between this spectral indicator value and k' is not linear, they are clearly related and suggest that correlations such as this can be uncovered with more systematic study. Similar studies on a series of alkylbenzenes and a homologous series of perdeuterated normal alcohols are being pursued to further elaborate such interactions.

Table 1. Correlation of I[□$_a$(CH$_2$)]/I[□$_s$(CH$_2$)] with k' for toluene in methanol:H$_2$O mobile phases.

I[□$_a$(CH$_2$)]/I[□$_s$(CH$_2$)]	k'	% H$_2$O
1.35 ± 0.02	0	0
1.24 ± 0.02	0.9	25
1.18 ± 0.04	5.6	50

Raman Spectroscopy of Ion Chromatography Systems.

Important ion chromatography methods include ion exchange chromatography, complexation ion chromatography, ion pair chromatography, and extraction chromatography among others. We have recently begun to explore the utility of Raman spectroscopy for probing the molecular basis of ion retention in ion exchange systems. Although only a few results are in hand, they clearly support the notion that Raman spectroscopy can provide useful molecular-level information about ion chromatographic systems. The data in the figure below are a demonstration of this potential for a trimethylpropyl quaternary amine strong anion exchange stationary phase covalently bonded to a silica support. The Raman spectrum of this stationary phase material was monitored in the presence of three different anions, Cl$^-$, Br$^-$, and I$^-$, in aqueous media at pH 6 and Raman spectral indicators of anion interaction with the amine were sought. As the plot in the figure shows, the frequency of the <(CH$_3$) mode from the methyl groups attached to the quaternary amine nitrogen is quite sensitive to perturbation of its chemical environment. This stationary phase is prepared and provided with a Cl$^-$ counterion such that the spectrum in its dry state reflects that of the quaternary amine-Cl$^-$ salt. In this form, the <(CH$_3$) is observed at ~3031 cm^{-1}. Upon immersion of this stationary phase material in slightly acidic water, the <(CH$_3$) mode shifts ~11 cm^{-1} to higher frequencies to ~ 3042 cm^{-1} presumably due to hydration of the ions. Furthermore, the frequency of this mode is quite sensitive to the nature of the anion to which the quaternary amine is binding, based on the shifts to lower frequencies by 2 and 6 cm^{-1} in the presence of Br$^-$ and I$^-$ in solution, respectively, relative to Cl$^-$. Of perhaps greater significance is the observation that the spectral change is almost linear with ion selectivity. The inverse correlation reflects the fact that the I$^-$ is retained more strongly than Br$^-$ that in turn is retained more strongly than Cl$^-$ due to the poorer hydration of the two larger anions in water than Cl$^-$. The presence of this correlation suggests that insight into the molecular basis that governs selectivity in this strong anion exchange system can be gleaned from Raman spectroscopic studies such as these. Since these types of chemical interactions form the foundation of all ion chromatographic methods, and since they have been studied very little with molecularly-specific surface vibrational spectroscopies under chromatographically-relevant conditions, we intend to extend our investigations to other types of ion chromatographic systems including extraction chromatographic and complexation ion chromatographic systems to develop a broader understanding of the general applicability of this approach.



HEAVY ELEMENT AGGREGATION PHENOMENA

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Overall research goals:
The objective of this research is to develop a fundamental molecular-level understanding of the interactions and forces that drive and limit the aggregation of heavy element species. Our emphasis is on self- and directed assembly processes in which phosphorus-based complexing agents (both organic and inorganic) strongly interact with heavy element ions in liquid and glass phases. We seek to establish the knowledge base that is essential for assessment of self- and directed assembly for creation of novel catalysts, sensors that are stable at high temperature, and advanced concepts for nuclear fuel processing and disposal, as well as to improve understanding of the constraints that arise due to aggregation in present and proposed solvent extraction processes.

Specific objectives for 2002-2003:
Self-Assembly of Aggregates: Small-angle neutron scattering (SANS) measurements indicate that scattering intensity increases sharply upon extraction of increasing amounts of solutes into the organic phase. These results, when interpreted with a model involving only aggregate size growth in solution when phase splitting is approached, lead to unrealistic results. By using available approximate theoretical treatments, we intend to demonstrate that the increase in scattering is better explained by interactions between small reverse micelles rather than by aggregate size growth.

Directed Assembly of Aggregates: The influence of heavy metal and phosphate ions on pore collapse and pore coalescence of silica will be determined using conventional and anomalous small angle X-ray scattering techniques along with a broad array of atomic and molecular spectroscopies the basis of which are photons whose energies range from a few thousands to several electron volts. Heavy metal-to-phosphorus ratio and the thermal densification cycle will be varied to generate the knowledge base that is essential for future theoretical modeling of heavy element anomalous small angle X-ray scattering as well as molecular dynamics calculations on the resultant heavy metal phosphate nanophases.

Significant achievements:
Self-Assembly of Aggregates: We have revisited third phase formation in the HNO_3-$UO_2(NO_3)_2$ or $Th(NO_3)_4$, TBP-*n*-alkane systems focusing on solute aggregation (TBP = tri-*n*-butylphosphate). Visible and IR spectroscopy and EXAFS measurements have provided information on the coordination of metal nitrates and HNO_3 to TBP in the organic solution (1-3). SANS measurements on TBP solutions loaded with progressively increasing concentrations of HNO_3 and metal nitrates, when interpreted neglecting the contribution of the structure factor,

indicated the presence in solution of aggregates containing up to about 40 TBP monomers (4). However, there is little precedence in the literature for the existence of such large aggregates.

Directed Assembly of Aggregates: Using the Actinide Facility and an insertion device beamline at the Advanced Photon Source at Argonne National Laboratory, we have established the power of anomalous small angle X-ray scattering (ASAXS) for the investigation of heavy element nanophases that are embedded in amorphous phases. Our initial ASAXS study on a mixed heavy metal ion-doped chemically functionalized porous silica showed that thermally promoted pore collapse and coalescence created heavy metal phosphate nanophases that contain a statistical mixture of the dopant metal ions thereby advancing our understanding of directed assembly as the basis for creation of tailored heavy element-based nanophases.

Plans for future research:
Self Assembly of Aggregates: Our future program consists in testing the generality of the intermicellar interaction model by investigating third phase formation in systems involving: 1) cations with different ionic potentials; 2) mineral acids with different hydration properties of the anion; 3) extractants with different basicities of the donor groups and different alkyl groups; 4) multidentate extractants; 5) co-solvents and solvent modifiers, such as long-chain alcohols, aromatic solvents, surfactants and ionic liquids.

Directed Assembly of Aggregates: To establish the knowledge basis that is essential for assessing directed assembly for creation of novel catalysts, high temperature stable sensors and new concepts for nuclear waste processing and disposal, we will create and characterize the heavy metal phases that result from atom-by-atom assembly of complexes that further aggregate into nanophases with an emphasis on heavy metal phosphates in vitreous silica. We will probe the processes that create these phases as a function of length scale using state-of-the-art techniques such as ASAXS and pair distribution function measurements, as well as more conventional techniques such as XANES/EXAFS, XRD, SANS, LIF, Raman, FTIR, and MAS-NMR. Our studies will be informed and guided by complementary theoretical modeling that includes approaches such as molecular dynamics calculations.

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Abstract P2-5

NMR Studies of Structure and Gas Binding in Molecular Sieves

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Overall research goals: We aim to (I) use ^{17}O MAS NMR, in combination with MQMAS and double resonance methods, to study gas binding in separations and catalysis, (II) develop new NMR approaches to quantify the separation between catalytic or binding sites and for studying interactions between catalytic sites and (III) apply our newly-developed NMR methodology to novel separations materials.

Specific objectives for 2002-2003:
Complete our ^{17}O NMR studies of zeolites with Si/Al ratios of 1.
Develop new probe molecules with two basic end groups to study acidity
Complete our NMR experiments on the lithosilicates and copper aluminum chlorides.

Significant achievements:
(I) ^{17}O MAS NMR and MQMAS NMR Studies of Zeolites: We have been exploring the use of ^{17}O MAS NMR Spectroscopy as a probe of gas-surface interactions, as part of our NMR effort to develop methods for studying gas binding in molecular sieves and on surfaces. Our initial work has focussed on zeolites with Si/Al ratios of 1 (zeolites A and LSX). These systems were chosen so that only Si-O-Al and no Si-O-Si oxygen environments are present, simplifying the assignments (somewhat). Our work on the cation-exchanged A zeolites has shown that simple correlations between oxygen bond angles and the ^{17}O isotropic shift are not valid for these systems.[1] Although the spectra are non-trivial to analyze, they contain a wealth of potential information concerning the nature of sorbent/sorbate interactions. Changes in the extraframework cation or the presence of hydrogen bonding to water or sorbed molecules produce significant differences in chemical shift, but do not noticeably affect the quadrupole coupling constants (QCCs) of the oxygen sites. We have used double resonance experiments such as ^{17}O/^{23}Na TRAPDOR and ^{1}H/^{17}O CP NMR spectroscopy to help assign the resonances and probe for H-bonding

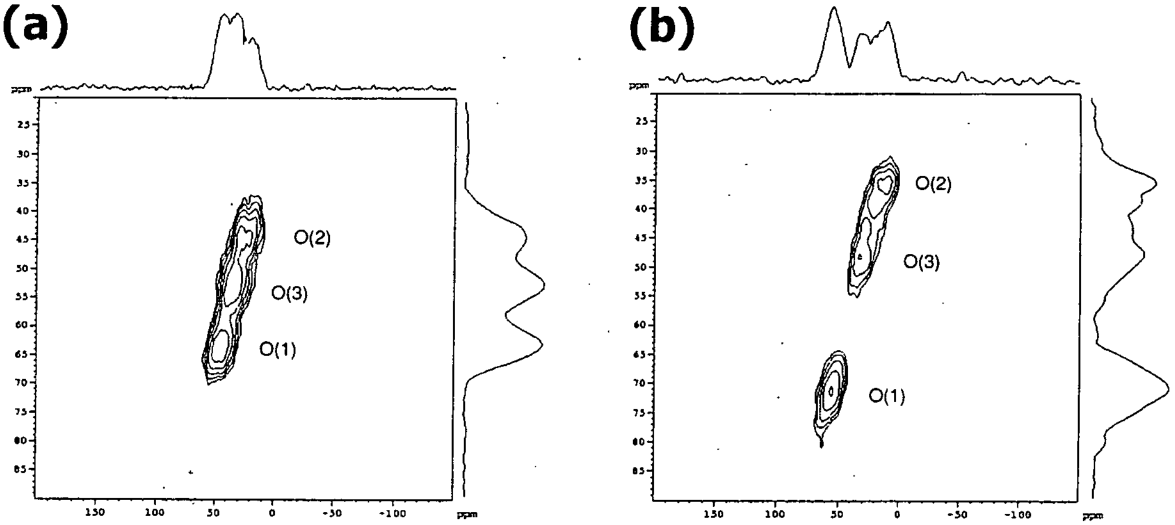

Figure 1. Two-dimensional, triple-quantum, ^{17}O MQMAS NMR spectra of (a) hydrated and (b) dehydrated CaA after shearing showing the strong effect of hydration level, particularly on the O(1) resonance in the 8-ring of the zeolite.

interactions. Our studies have now been extended to Y zeolites, which contain Si-O-Si and Si-O-Al linkages. The results demonstrate that these linkages can be readily resolved in a variety of cation-exchanged zeolites, since the QCCs of the oxygen atoms in the Si-O-Si linkages are much larger than those containing Al.

(II) New NMR approaches for quantifying the separation between catalytic or binding sites and for studying interactions between catalytic sites: To initiate this new program, we have chosen to study the following series of probe molecules, $Ph_2P-(CH_2)_n-PPh_2$, where n varies from 1 to 6. Phenyl-containing systems were selected, so as to minimize the mobility of the phosphines on a surface or in the pores of a zeolite. These probe molecules can fit in large pore zeolites such as the faujasites. These molecules have been used to quantify the separation between acid sites and to study acidity in zeolite HY.

(III) Sorption and Separations in Novel Zeotypes: Studies of two new classes of materials have been completed in this grant period, namely lithosilicates and copper aluminum chlorides. We have shown that high resolution ^7Li and ^6Li NMR spectra may be obtained from the lithosilicates by using high magnetic field strengths (16.3 T). For example more than seven resonances were observed for the zeolite RUB-29, allowing us to determine which Li^+ sites are removed during ion-exchange with Cs^+. Furthermore, the lithium-shift could be correlated with the bond-valence sum and a correlation between bond-valence sum and ease of ion-exchange was established.[2]

Plans for future research on this project:

We now propose to examine the effect of gases such as chloroform or acetone, which can hydrogen-bond strongly to the zeolite framework or to the Bronsted acid sites, on the ^{17}O NMR spectra of a series of X and Y zeolites. The diphosphines will be sorbed in faujasite zeolites with much lower Bronsted acid concentrations and samples containing both Bronsted and Lewis acid sites. More sophisticated NMR experiments will be used to determine the which silicon sites, $Si(OSi)_n(OAl)_{4-n}$, are bound to the protonated phosphines. Finally, the NMR methodology will be used to characterize a series of novel molecular sieves.

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Abstract P2-6

The Chemistry of Rutherfordium and Dubnium (Elements 104 and 105)

Heino Nits**The Chemistry of Rutherfordium and Dubnium (Elements 104 and 105)**

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Overall research goals:

Studies of the chemical properties of the elements are among the most fundamental goals in chemistry. Our world-leading studies of the chemical properties of the transactinide elements (Z=104-108) are unique within the US. Comparison of heavy element chemical properties with those of periodic table homologs and with theoretical predictions provides important insights for a better understanding of chemical properties throughout the periodic table and of yet unstudied elements.

Student training in ultra-sensitive nuclear physics and chemistry techniques: These exotic, frontier studies attract many undergraduate and graduate students to nuclear and radiochemistry. This research provides excellent education and training for future contributions and careers in a variety of applied areas, as well as in frontier research. Applied areas include:predicting and monitoring of behavior of actinides in the environment; nuclear medicine and isotope production; radio-pharmaceutical preparation; nuclear power, nuclear waste isolation and site remediation; treatment, processing, and minimization of wastes; ultra-sensitive instrumentation and analyses; automated and computer-controlled remote processing; and stockpile stewardship and surveillance of clandestine nuclear activities.

Specific objectives for 2002-2003:

To investigate some of the fundamental liquid-liquid extraction chemistry of elements 104, rutherfordium, Rf, and 105, dubnium, Db.

To study if relativistic effects predicted for the heaviest elements exert anomalous trends in ionic radii, stabilization of different oxidation states, and otherwise unexpected trends in complexation behavior and chemical bonding relative to lighter homologues.

Significant achievements:

In collaboration with scientists from the University of Oslo, GSI, University of Mainz (both Germany), and Chalmers Technical University (Sweden) with the SISAK rapid chemical extraction and liquid scintillation detection system coupled with the BGS as a pre-separator. A proof-of principle experiment was performed, where 4.5-sec ^{257}Rf was produced in the ^{208}Pb(^{50}Ti,n) reaction. After separation from other reaction products with the BGS, the Rf atoms were transported to the SISAK on-line liquid-liquid extraction system. After chemical separation of the ^{257}Rf, alpha decay of ^{257}Rf, and the short-lived ^{253}No and ^{249}Fm daughters were measured by liquid scintillation pulse height spectroscopy. These experiments demonstrated an important new capability in transactinide chemical separations, where well-understood liquid-liquid extraction techniques can be used to study chemical properties of transactinide isotopes with half-lives of only seconds, and production rates of only a few atoms per hour.

Experiments presently in progress are testing new developments in the liquid scintillation detector system. Waveform digitizers are used to better distinguish between alpha particles and the conversion electrons that often accompany them. These experiments will continue with measurements of chemical properties of 4-s ^{257}Rf and 4-s ^{258}Db, produced in the ^{208}Pb(^{50}Ti,n)^{257}Rf and ^{209}Bi(^{50}Ti,n)^{258}Db reactions, respectively. In other SISAK-related work, several liquid-liquid extraction systems have been tested in batch mode with Hf and Zr (periodic table homologs of Rf) to find extraction systems with relatively low acid concentrations, and fast kinetics, which could be used for Rf chemistry with SISAK.

Plans for future research on this project:

BGS-SISAK rapid transactinide chemical separations: Chemical properties of Rf (element 104) and Db (element 105) will be measured using the BGS coupled with the SISAK chemical separation system. The pre-separation from interfering radioactivity with the BGS relaxes many constraints on the choice of chemical separation systems, allowing the use of chemical systems that are more selective within the respective groups of the periodic table. With the impending closure of the LBNL 88-Inch Cyclotron, we will relocate the BGS to another high-intensity heavy ion accelerator, and we expect only a short break in the related transactinide chemistry program.

Development of extraction systems for the study of rutherfordium: The success of our physical pre-separation system prior to conducting chemistry experiments leads not only to a reevaluation of previously used extraction systems, but allows also the use of a different class of extraction systems in future experiments with the SISAK system or other fast automated chemistry systems. The selectivity between the members of the same group of the periodic table can now be favored over efficient separation from elements belonging to other groups when designing extraction systems for future experiments.

We are evaluating different extraction systems for their usefulness to study the chemical properties of rutherfordium. Traditionally extraction systems for liquid-liquid extraction experiments were chosen to separate the nuclide of interest from interfering activity, but not necessarily to be selective between the homologues of a transactinide element. On-line experiments with the lighter homologues of Rf are necessary to determine the selectivity of different extraction systems in addition to the usual batch experiments. Experimental conditions can affect the kinetics of the extraction and thus have a large influence on the distribution ratios studied. We are studying the extraction behavior of hafnium from hydrochloric acid and thiocyanate media with different organic extractants such as dibenzo-18-crown-6, methyl isobutyl ketone and tributyl phosphate

Toward organometallic chemistry of transactinides: We are expanding the knowledge on the chemical behavior of the transactinide elements to organometallic compounds, a class of compounds that have not been investigated so far. This project proposes the first investigation of an organometallic compound with the transactinide element rutherfordium, Rf. Future studies will also include heavier transactinides since the basic experimental system will be relatively easy to adapt to other similar chemical systems. This study will shed further light on the influence of relativistic effects in the chemistry of the heaviest elements in addition to those gained in past gas chemical studies as well as those observed in the aqueous phase.

Abstract P2-7

Advancing the Capabilities of Surfaced Enhanced Raman Scattering in Chemical Analysis

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Overall Research Goals: Despite the impressive recording of spectra for single molecules of a few highly Raman active species, fortuitously positioned at "hot spots" on random substrates, certain persistent fundamental limitations of SERS have significantly lessened the impact of the technique in chemical analysis. The overall goal of this research project is the fundamental development and practical utilization of novel functionalized polymer-noble metal composite substrates that provide high levels of electromagnetic SERS enhancement for a wide range of analytes. The substrates are primarily designed to provide a means to perform information-rich detection in capillary electrophoresis (CE) methods of separation,[1,2] although high-throughput methods of analysis and advanced sensing approaches should also benefit from the creation of these nanocomposite materials. The project includes computational studies of electromagnetic enhancement[3] and analyte receptor interactions,[4,5] the creation of new receptors for sequestering analytes,[6,7] new approaches to generating versatile substrates,[8,9] and efforts to improve the analytical figures of merit of SERS.[8]

Specific Objectives for Current Year: This presentation and objectives of this year focus on the creation and evaluation of pliable polydimethylsiloxane (PDMS) – silver nanocomposite materials as SERS substrates. Pliable polymer-nanometallic particle composites have technological potential due to their unique optical and electrical properties. Physical vapor deposition of silver metal onto PDMS was performed. Rapid Ag diffusion and particle formation in a phase separated surface layer of the PDMS creates unique sub-surface-based composites that vary in properties based on rate of deposition and average Ag thickness. Nano-metallic particle spacing can be altered in a reversible manner by physically manipulating the Ag-PDMS composite. The optical properties of the materials were studied by visible wavelength optical extinction spectrometry and SERS, including studies during physical manipulation (see Figure 1).

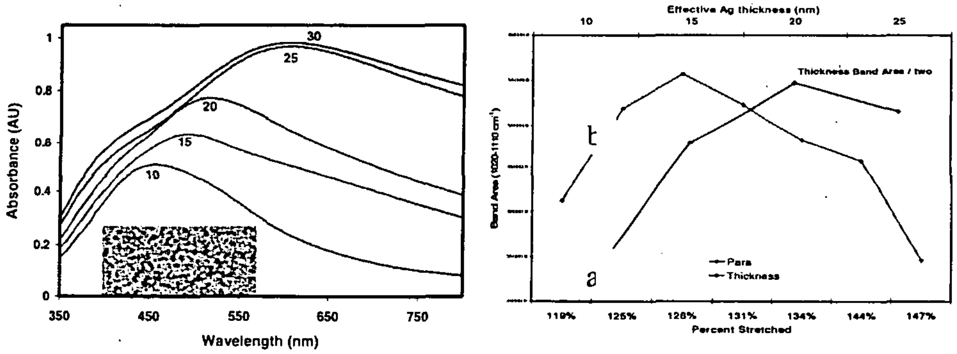

Figure 1. At left, the effect of average Ag thickness on extinction curves is provide as well as an SEM insert at 90K magnification showing fairly regular ~ 100 nm particles that XPS depth profiling indicate are slightly embedded in the phase separated layer creating a quisi-3D structure. On the right, the SERS activity (an aminothiophenol band is plotted, excitation at 633 nm) exhibits a maximum (a) at ~ 20 nm thickness (DC conductivity measurements indicate the percolation threshold is at ~ 40 nm). The figure also demonstrates the unique ability to change optical properties by physical manipulation; 18 nm average thickness Ag was deposited onto a PDMS film stretched to about 1.5 times its relaxed length. As the film is allowed to relax, a maximum in SERS activity is seen as well (b).

Significant Achievements:

- Off-column SERS detection in CE was demonstrated for the first time.[2]
- Electromagnetic modeling of optical responses of Ag nanoparticles was performed and used to explain SERS behavior for measurements performed under liquid nitrogen.[3]

- New cyclodextrin receptors were synthesized for use in sequestering analytes.[4,5]
- Molecular modeling techniques were refined to assist in designing and characterizing receptors.[6,7]
- The optical properties of PDMS-Ag were studied and revealed the potential of the composites as substrates for (i) high and tunable SERS activity, (ii) an ability to concentrate analyte while also protecting the noble metal from oxidation, and (iii) molding into functional devices.[8,9]
- The quantitative and qualitative reproducibility of SERS was substantially improved via the development of a sample translation technique.[8]
- SERS was demonstrated in levitated droplets for the first time.[10]

Future Plans: During the coming year we will extend the chemical nature of the polymer-metal nanocomposites to include Au, other polysiloxane additives, and, time permitting, attempt to employ molecular imprinted polymer systems. The PDMS-Ag composites will be molded into microfluidic devices and evaluated as integrated (separation and detection) platforms for CE-SERS. Our theoretical models for the optical response of systems of coupled metal nanoparticles will be extended to treat multi-particle systems that better mimic the local structures typical of the PDMS-metal composites (see Figure 1 insert). We will begin attempts to bring order to our nanometallic architectures using more straightforward nanolithographic methods such as the nanosphere lithography technique of Van Dyne or by creating structures using focused ion beam milling.

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Creating Isotopes of Elements 114, 116, and 118 — The Essential First Step to Their Chemical Characterization

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Overall research goals: We intend to produce longer-lived isotopes of the elements occupying the island of enhanced stability, namely elements 114 through 118 [1-6], and to study their chemical properties. Currently, the emphasis of our research is on the production, mass assignment, and nuclear decay properties of the created isotopes. The investigation of the aqueous chemistry of these elements will be addressed in future experiments. Experimental chemistry data will help develop our understanding of the influence of the relativistic effects on the chemical properties of elements with $Z \geq 114$.

Specific objectives for 2002-2003: Within our Dubna-Livermore Collaboration (DLC), the following long-duration irradiation experiments had the highest priorities in FY 2002 and FY 2003: the irradiation of ^{249}Cf with ^{48}Ca was performed to produce ^{294}118 via the 3-neutron evaporation channel, resulting in a decay signature proceeding through the isotope ^{290}116. The reaction ^{245}Cm (^{48}Ca, 3n), which is currently running at Dubna, is designed to produce and characterize the decay properties of ^{290}116, the daughter of ^{294}118. The results of this experiment will be crucial for the soon to be run second irradiation of ^{249}Cf (^{48}Ca, 3n) ^{294}118. If we detect a couple of decay chains of ^{290}116 decaying through ^{286}114 in the ^{245}Cm + ^{48}Ca experiment, detecting just a single atom in the ^{48}Ca bombardment of ^{249}Cf would be sufficient, provided its characteristics coincide with those produced in previous experiments. Furthermore, a planned irradiation of ^{243}Am with ^{48}Ca will be performed to produce isotopes of the unknown elements 115 and 113, to identify their nuclear decay properties, and to determine whether alpha decay across the Z=114 proton shell can be observed as a reduction in alpha-decay energy. All irradiation experiments will be performed at JINR, Dubna, Russia using either the Dubna Gas-Filled Separator (DGFS) or the kinematic separator (VASSILISSA).

The chemical characterization of the elements with $Z \geq 112$ is challenged by the isotopes short life-times and also by their extremely low production rates of one-atom-per-week or even per-month. A thorough literature review (to be submitted), pertaining to the chemical properties observed in group-14 elements, is our first step in guiding the development of an aqueous identification scheme based on the newest sensor and detector technologies. Another pathway the

DLC is currently pursuing is the development of a new separator (*MASHA - Mass Analyzer of Super Heavy Atoms),* capable of identifying the mass number of the created and separated isotope to less than ¼ amu. Our responsibilities within the MASHA project as part of the DLC include the design of a high-temperature, diffusive plutonium target and collaboration in design and construction of the detection system. Currently the existing literature is being reviewed to identify the most suitable plutonium ceramics that withstand temperatures of at least 2000°C without releasing the plutonium itself but allowing the diffusion of the reaction products out of the matrix. We are currently also testing new amplifier-preamplifer modules for their suitability in the detection system to be set up for MASHA.

Significant achievements: Employing the DGFS and the U400 cyclotron in Dubna, we attempted the synthesis of element 118 in the reaction $^{249}\mathrm{Cf}\,(^{48}\mathrm{Ca}, 3n)\,^{294}118$; we detected two events that may be attributed to the formation and decay of nuclei with Z=118[6]. During a 2300-hour irradiation, the $^{249}\mathrm{Cf}$ target (0.23 mg/cm^2) accumulated a total beam dose of 2.5×10^{19} $^{48}\mathrm{Ca}$ ions at an energy of 245 MeV. Preliminary results show that one event decays through a chain of two correlated α-decays with corresponding energies and correlation times of $E_{\alpha1}$=11.65±0.06 MeV, $t_{\alpha1}$=2.55 ms and $E_{\alpha2}$=10.71±0.17 MeV, $t_{\alpha2}$=42.1 ms and, finally, a spontaneous fission with the sum of the kinetic energies of the fission fragments E_{tot}=207 MeV (TKE~230 MeV) and t_{SF}=0.52 s. The second candidate event consists of a recoil nucleus fissioning with E_{tot}=223 MeV (TKE~245 MeV) 3.16 ms after implantation. The probability that those events were caused by chance correlations of unrelated signals is negligible[3]. Both events were observed at an excitation energy of the compound nucleus $^{297}118$ of E^*=30.0±2.4 MeV, close to the expected maximum for the $3n$-evaporation cross section. The relationship between the decay energy Q_α and decay period T_α shows that sequential α-transitions in the first event match those expected from the decay chain $^{294}118\rightarrow{}^{290}116\rightarrow{}^{286}114$.

Plans for future research: Although current experimental results on elements 114, 116, and 118 are significant in proving the concept of enhanced stability at Z=114, these experiments do not provide chemical evidence for the elemental identification. Furthermore, the Z-assignment of these new elements is not conclusive since their decay chains are not anchored in known isotopes. Our future research goals include providing conclusive evidence for the Z-assignment of the created atoms either by chemically identifying the produced element or by providing a mass assignment together with a decay signature. The latter will be achieved by utilizing the newly developed MASHA device.

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The work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

Abstract P3-1

Details of Ion Hydration and Ion-Pair Structure from X-ray Absorption Spectroscopy and Molecular Dynamics Simulations

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Overall research goals: Our goal is to determine the molecular-level structure of ion hydration and ion-ion interactions in water and to improve models of these systems. By conducting these experiments over a wide range of temperatures, it is possible to modulate the amount of cation-to-anion coordination without changing the chemical composition of the systems. At moderate- to low concentrations and under ambient conditions, most cations and anions are fully dissociated. However, at high temperatures the contact-ion pairs form. Thus, for aqueous systems containing simple salts, one can explore both the hydration and the contact-ion-pair chemistry. These results have far reaching implication for all aqueous systems in the area of chemistry, biochemistry, environmental and geochemistry.

The method used in this characterization is x-ray absorption fine structure spectroscopy (XAFS) which accurately measures the first-shell structure about ions. Only recently has the utility of this technique been realized for probing aqueous systems well above 200°C. In ongoing studies we are using XAFS to study the structure of supercritical water at the Advanced Photon Source at Argonne National Laboratory. In the first studies of this kind we have shown that XAFS is a powerful method to determine the local solvent environment around an ion in terms of the number of nearest solvent neighbors and the hydration distance.

Another extremely important outcome of the research is that we have developed ways to test and improve intermolecular potentials that are used in simulations. These ion-water and ion-ion intermolecular potentials are used both for high-temperature and ambient water studies. The existing water models fail to accurately predict certain aspects of the structure in ambient water and their performance for high-temperature water is much worse. From the XAFS experimental results we have implemented improvements to these models that have significantly boosted their performance by use of more realistic potentials. The development of more accurate water-ion potentials will have a profound impact on a broad range of disciplines.

Specific objectives for 2002-2003: Many different ion-water systems have been studied with XAFS starting with an early landmark investigation of Sr^{2+} in supercritical water. We have found significant dehydration occurring under supercritical water conditions for mono- and di-valent cations (Sr^{2+} and Rb^{+}) and for a monovalent anion (Br^{-}). More recently we have explored the fascinating changes in the coordination structure that occur for ion-pair species of the transition metal, Ni^{2+} and Cu^{1+}. In the most recent studies, we have produced a definitive study of Ca^{2+} and Sr^{2+} hydration under ambient conditions. The Ca^{2+} structure was derived from a collaborative project with Mike Simonson of the Chemical and Analytical Sciences Division at Oak Ridge National Laboratory. In this study several different $CaCl_2$ solutions were measured under identical condition using our XAFS method at the Advance Photon source and then the ORNL neutron diffraction with isotopic substitution (NDIS) method at Institut Laue-Langevin. The Ca-O and Ca-H bond distances are in perfect agreement with the NDIS values providing the first independent verification of this structure. A remarkable finding of our work is that a recent refinement of the ab initio XAFS code (FEFF8) now properly treats the H scattering of the first shell water molecules thus generating a Ca-H distance corresponds to a water tilt angle of 47° on the surface of the ion.

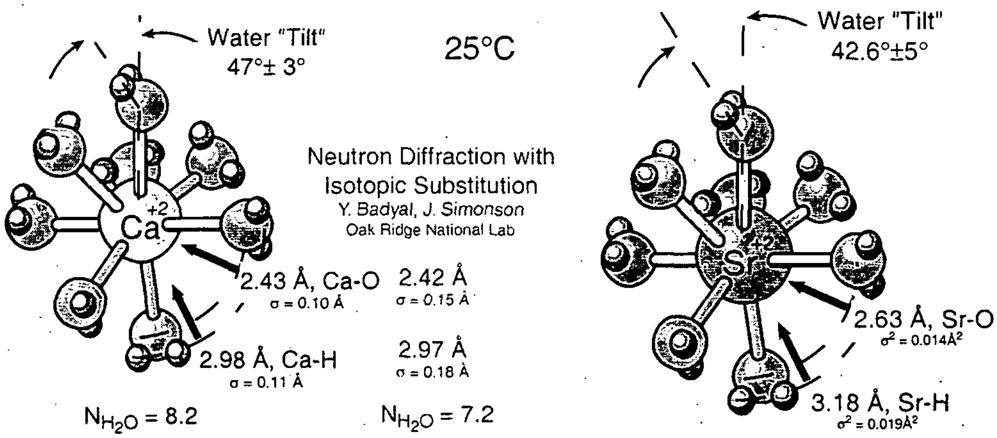

Figure 2. A comparison of water structure about Ca^{2+} and Sr^{2+} from XAFS and NDIS

Significant achievements: From a detailed evaluation of XAFS, NDIS, MD and ab initio results we are developing more accurate models of ion-water structure. Ion-water potential models fail to completely capture first-shell hydration structure. For instance, the width of the first peak in the Ca-O pair distribution function is about 50% smaller than what we measure experimentally. Existing models describing ion-ion interactions are even less accurate, failing to predict both the bond distance and bond strengths. Our collaborators are working with us to refine potentials based upon these results.

Plans for future research on this project: We are moving on to XAFS studies of low-Z atoms, such as K, and Cl. These studies will be compared to a huge body of simulation literature on both ambient and high-temperature KCl systems. We expect to capture the first information on K^+/Cl^- ion pair structure. We will continue both MD and ab initio studies for direct comparison to experimental XAFS systems.

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Abstract P3-2

Actinide Incorporation and Radiation Effects in U(VI) Solids

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Research goals: This project investigates the processes and mechanisms by which the U(VI) solids incorporate other cations, particularly actinides and fission prodcuts. These U(VI) solid phases are the alteration products of spent nuclear fuel under oxidizing conditions.. This research provides fundamental information on the formation of solid solutions of the U(VI) solids, studies their capacity to accommodate other non-U cations, and elucidates the effects of ionizing radiation on the alteration products of of the UO_2 in spent nuclear fuel.

Objectives include:

- Determination of the mechanisms of transuranium element substitution into select U(VI) solid phases, and the determination of the role of solution speciation in the formation of U(VI)-actinide solid solutions;
- Determination of the effect of ionizing radiation and alpha-decay event damage on the structure and stability of uranyl phases.

Specific objectives for 2002-2003: We have investigated two hypotheses.

Hypothesis 1: *The various oxidation states of the non-uranium f-elements can be substituted into the U(VI) oxide hydrates, and U(VI) silicates, but the location(s) for substitution depend on the coordination requirements for each specific f-element oxidation state.*

Valence bond calculations completed for the U(VI) silicate structures indicate that the oxidation state and local coordination of the non-U *f*-element will determine where these cations can be accommodated in the U(VI) solid phases. For example, the dioxo cations should be accommodated within the structure by substitution for the uranyl cation. The trivalent actinides are not expected to fit easily into positions occupied by the uranyl cation, but rather into spaces typically occupied by monovalent and divalent cations (e.g., Na^+ or Ca^{2+}). Synthetic α-uranophane was prepared, except that some or all of the Ca^{2+} used in the synthesis is replaced by another non-U *f*-element cation. The other cations used thus far include Eu^{3+}, Th^{4+}, and NpO_2^+. The resulting materials are characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Variables include the mole fraction of Ca^{2+} replaced by other cations and the amount of time the material is aged prior to characterization.

In most cases, we see that the non-Ca^{2+} cations are removed from solution immediately, and are associated with the bulk solid phase. The initial crystallinity of the solid phase decreases with increasing substitution of the non-Ca^{2+} cation (compared to synthetic uranophane). With time, the crystallinity of all the solids increases. SEM and TEM show, however, that the solids formed are actually mixtures of phases. Needle-like α-uranophane crystals are observed along with other very finely divided, poorly crystalline solids into which the non-Ca^{2+} cation tends to be preferentially incorporated.

<u>Hypothesis 2</u>: *Radiation (elastic and inelastic) effects will have a considerable impact on important properties associated with the incorporation of trace-elements into uranyl phases. These include: solid-state amorphization, phase decomposition, radiation-enhanced diffusion, solute segregation, cation-exchange and sorption capacity, defect migration and the formation of grain boundaries, recrystallization, and radiolysis.*

Here, we have been studying the effect of ionizing radiation on α-uranophane, and the non-Ca^{2+} analogues of α-uranophane. Using the materials prepared above for the incorporation studies, the solids are subjected to varying doses of electron irradiations. Irradiations are designed to mimic alpha-recoil effects. Selected area electron diffraction (SAED) and high-resolution TEM (HRTEM) are used to study loss of crystallinity in the solids with increasing irradiation.

Compared to α-uranophane, we observe that there is an increase in amorphization dose with increasing atomic mass for the non-Ca^{2+} cations. This means that when cations of higher mass are used to replace Ca^{2+}, higher doses of electron irradiation are required to achieve equivalent amounts of amorphization. Temperature is also an important parameter, with the temperature dependence of amorphization dose for α-uranophane indicating two stages: one occurring at temperatures $\leq$ 413 K and the other occurring at temperatures above 413 K. Interestingly, the loss of structural periodicity was not simply proportional to dose. Similar to electron-irradiated zeolites, the crystalline-to-amorphous transition required lower doses as the amorphous regions became larger. Results also suggest that water and OH^- may accelerate the formation of point defects in the solid during irradiation.

<u>Significant achievements:</u> Solid phases of the U(VI) silicates into which other non-U *f*-elements have been incorporated have been prepared and are being characterized. An interesting new "nano-phase" has been observed. In addition, their behavior under ionizing radiation has been studied.

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Abstract P3-3

Molecular Environmental Science Using Synchrotron Radiation: Chemistry and Physics of Waste Form Materials

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Overall research goals

Production of defense-related nuclear materials has generated large volumes of complex radioactive chemical wastes. Disposition of these wastes requires conversion of liquid and solid-phase components into durable, solid waste forms suitable for long-term immobilization. Special glass compositions and ceramics such as pyrochlores and apatites are the main matrices for these wastes. Performance of waste-form materials is determined by the loading capacity of the radioactive and non-radioactive waste constituents, and the long-term chemical and radiation resistance of the waste-form package to leaching (durability) is linked to local structure around the waste components. Equally important is local structure of the constituents comprising the glass or ceramic host matrix. Knowledge of structure of waste-form host matrices is essential, prior to and subsequent to waste incorporation, to evaluate and develop improved compositions. Detailed structural information also provides a basis to mechanistically understand durability.

The soft-x-ray synchrotron-radiation technique of near-edge x-ray-absorption fine structure (NEXAFS) is a unique method to investigate the oxidation state and structure of low-Z elements forming the backbones of these glass and ceramic host matrices. Light metal ions in ceramic hosts such as titanium also are ideally investigated by NEXAFS. Thus, our primary objectives are to understand light-element speciation in waste-form materials via NEXAFS and to translate this knowledge into better waste-form materials. Another aim is to investigate "real" waste-form materials. We have recently enhanced Beamline 6.3.1 of the Advanced Light Source (ALS) to conduct detailed structural investigations in pyrochlore-ceramic and borosilicate-glass materials.

Research objectives for 2002-2003

Investigation of structurally related issues in pyrochlore ceramics will continue and polarization-dependent NEXAFS studies will be completed. Boron speciation in several new glass series will be determined and correlated to observed durability properties. Characterization of ALS Beamline 6.3.1 will be completed and a scientific manuscript describing its attributes submitted.

Significant Achievements

Use of ceramic pyrochlores as host matrices for actinide-rich wastes has received increasing attention since recent discoveries showed isovalent substitution of Zr for Ti in $Gd_2Ti_2O_7$ results in an increase of 4 to 5 orders of magnitude in resistance to energetic-particle irradiation. Cation disorder and accompanying anion Frenkel defects are the main cause for a dramatic increase in oxide-ion conductivity and radiation tolerance in ordered pyrochlore-structured oxide materials, but there is limited direct experimental evidence on cation antisite disorder in what would normally be highly ordered structures. We have done Ti-2*p* and O-1*s* NEXAFS and x-ray-photoelectron spectroscopy (XPS) investigations to elucidate the mechanism leading to cation disorder and anion Frenkel defects. These studies show Ti^{4+} ions in $Gd_2Ti_2O_7$ pyrochlore occupy octahedral sites with a tetragonal distortion induced by vacant 8*a* oxygen sites located in the *ab* plane adjacent to TiO_6 octahedra. The coordination of Zr increases from 6 to nearly 8 with increasing substitution of Zr for Ti in $Gd_2(Ti_{1-y}Zr_y)_2O_7$. Oxygen anions migrate either from occupied 48*f* or 8*b* sites to vacant 8*a* sites to compensate for the increased Zr coordination [1-2].

The mechanism and structural properties leading to this superior radiation resistance also has been characterized. Effects of ion-beam irradiation of increasingly Zr-substituted pyrochlores have been followed by NEXAFS and XPS [3]. Irrespective of Zr concentration, a phase transformation occurs from the ordered pyrochlore structure (*Fd*3*m*) to the defect fluorite structure (*Fm*3*m*) following 2.0-MeV Au^{2+} ion-beam irradiation of $Gd_2(Ti_{1-y}Zr_y)_2O_7$. The irradiated $Gd_2(Ti_{1-y}Zr_y)_2O_7$ with $y \leq 0.5$ are amorphous, but possess significant short-range order. In contrast, compositions with $y \geq 0.75$ retain their crystallinity after ion-beam irradiation. The structures of Zr^{4+} in the irradiated $Gd_2(Ti_{1-y}Zr_y)_2O_7$ with $y \geq 0.75$ are almost the same as in cubic fluorite-structured yttria-stabilized zirconia (y-ZrO_2), providing solid evidence for the phase transformation. Rearrangements of oxygen anions amongst 48*f*, 8*b*, and 8*a* sites and of cations between the 16*c* and 16*d* sites in ordered $Gd_2Ti_2O_7$ require more energy compared to the relatively less-ordered pyrochlore-structured $Gd_2Zr_2O_7$. The XPS data show a single narrow peak at 529.6 eV with FWHM of ~1.5 eV characteristic of surface Ti-O (48*f*) in $Gd_2Ti_2O_7$.

Most of the experimental investigations have been performed at ALS Beamline 6.3.1, an entrance-slitless bend-magnet beamline with a Hettrick-Underwood-type varied-line-space grating monochromator operating from 200 to 2000 eV. For the waste-form NEXAFS studies, an improved beam-intensity (I_0) monitor was implemented, a fluorescence-detector system was installed, a low-temperature sample-stage was fabricated, and extensive characterization and optimization of the beamline optics was conducted to permit state-of-the-art NEXAFS measurements [4].

Plans for Future Research

The focus will remain on a range of scientific issues pertaining to light-element speciation and structure in ceramic and glass materials. The approach to obtain this information will continue to use NEXAFS and XPS. An x-ray-emission spectrometer is nearing completion and will be used to address new and more-detailed avenues in waste-form science. New investigations of glass materials will be started based on a recent collaboration with Catholic University of America.

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Abstract P3-4

The Actinide Facility

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Overall research goals: The two synergetic goals of this program are to (1) provide an infrastructure and support for researchers wishing to perform experiments on actinide-containing samples at ANL's Advanced Photon Source (APS); and (2) design and demonstrate the application of new synchrotron techniques to the actinide community. The experiments currently available to users include standard x-ray absorption spectroscopy (XAS), as well as in situ spectroelectrochemistry, high-energy scattering, small-angle scattering, and diffraction. The Facility has safety protocols, sample-containment boxes approved by the APS, and in-house expertise, all of which are available to APS users on a prearranged basis.

Specific objectives for 2002-2003: We will continue our efforts to provide support for experiments on actinide-containing samples at the APS, assisting users, and lending guidance on safety protocols, sample containment and hardware, and transport issues. Our technical efforts are focusing on the refinement of our electrochemical-cell design to permit high-energy and small angle scattering experiments. We also will set-up capabilities for analyzer-crystal XAS experiments and continue to develop high energy scattering (HES) and small-angle x-ray scattering (SAXS) experiments for actinide-containing samples of interest to the community.

Significant achievements: We have focused on developing our unique strengths, which include the ability to do chemistry in the synchrotron beam, enabled by the juxtaposition of our hot-laboratory facilities and the APS. This work has focused on the development and execution of electrochemistry experiments that are monitored in situ by the x-ray beam [1-5]. The combined development of analyses that permit the extraction of a formal valence for the metal-ion [6] has resulted in opportunities to obtain data that, heretofore, have not been available. Other experiments have taken advantage of our ability to make a sample and measure it shortly thereafter. For example, our Facility was used to prepare Np(IV) colloids, which are known to age quickly, and XAS measurements were completed within 48 hours of their formation [7,8].

Another of our unique strengths centers on the high-flux of high-energy (>60 keV) x-rays available at the APS. Using a dedicated high-energy station, 12-ID-C, we have focused on developing data reduction and analyses programs tailored for actinide-containing solutions. These data provide information about actinide coordination in solution that complements our EXAFS capabilities. The important aspect of this work is that, under favorable circumstances, HES can be used to measure correlations out to distances of 10 Å and greater. In addition, coordination numbers can be determined with considerable accuracy. When HES data are simultaneously refined with EXAFS data, this accuracy can be to within about 0.3 coordinating ions. We have used this technique to propose a dynamic equilibrium of waters coordinating to the uranyl ion in perchlorate solution [9].

Plans for future research on this project: Our primary focus for future research centers on (1) continuing to provide user support for experiments involving actinides at the APS; and (2) continuing to develop new synchrotron capabilities and demonstrating their success at addressing questions of interest to the actinide community. Future developments include hardware and data analyses packages for SAXS experiments, design and construction of a new spectroelectrochemical cell, and continued experiments on probing metal-ion aggregation using HES.

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Abstract P3-5

Sorption, Catalytic and Ion-Exchange Properties of Nanoporous Nickel Phosphates

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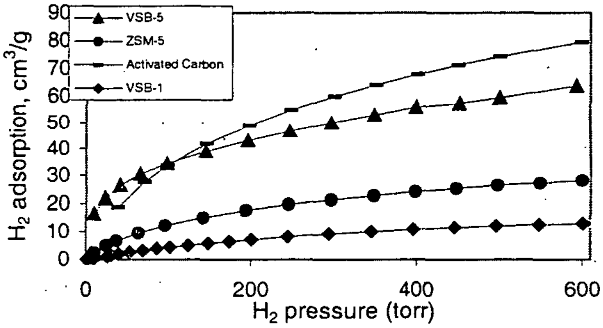
Overall Research Goals: The study of open-framework materials has traditionally been dominated by work on aluminosilicate zeolites, for the excellent reason that they find widespread applications in catalysis, separations and ion-exchange resins. However, since the discovery of nanoporous aluminum phosphates in 1982, and especially during the last decade, it has become apparent that many other classes of materials can be made in open-framework forms. Unfortunately, applications of these new materials have not been realized in most cases because it has proved impossible to render them truly nanoporous due to their poor stability. We have recently discovered a family of open-framework nickel phosphates that do have sufficient kinetic stability to be rendered nanoporous. These new materials have some remarkable properties that could have a major impact in several areas of materials science, particularly in the energy and environmental sectors. For example, they show excellent reactivity for shape-selective hydrogenation and dehydrogenation reactions, as well as remarkable hydrogen adsorption properties

Specific Objectives for 2002-2003: The first nickel phosphate systems were made in 1998 when AKC was on sabbatical leave in Versailles, France. The most interesting of these materials, to date, are the phases VSB-1 and VSB-5 (VSB=Versailles-Santa Barbara), both of which adopt hexagonal, honeycomb-like structure. VSB-1 has the approximate composition $K_4[Ni_{18}(HPO_4)_{14}(OH)_3F_9]\cdot 12H_2O$, but can also be made as the ammonium derivative.[1] Unlike other open-framework transition metal phosphates, it is truly zeolitic, being both ion-exchangeable and nanoporous. VSB-5, $Ni_{20}[(OH)_{12}((H_2O)_6][(HPO_4)_8(PO_4)_4].12H_2O$, is superficially similar, but differs from VSB-1 in that it has no ion-exchange capacity. In fact, charge neutrality requires not extra-framework cations but hydroxide ions in the framework, making it the first example of a truly basic 3D molecular sieve.[2] Its porosity is rather greater than that of VSB-1, with a surface area of up to 500 m^2/g (this is comparable to 1000 m^2/g for a zeolite on a per volume basis, since the density of the nickel phosphates is about twice that of aluminosilicates).

VSB-1 and VSB-5 have some remarkable properties that stem from the co-existence of nanoporosity and the presence of a redox center in the framework. VSB-1, for example, is bifunctional and will catalyze the cyclodimerization and dehydrogenation of butadiene to ethylbenzene.[3] VSB-5 on the other hand is an excellent catalyst for partial hydrogenation reactions, such as butadiene to butenes.[4] We are currently exploring other catalytic reactions, such as the hydroxylation of phenol. This work has been done in collaboration with Sang-Eon Park and Jong-San Chang at KRICT in Taejon, Korea. The reactivity of VSB-1 and –5 in hydrogenation and dehydrogenation reactions recently lead us to explore whether they might have potential for hydrogen storage. This work has benefited from a close collaboration with Dr. Juergen Eckert (LANL), who has been on part-time secondment to UCSB since early 2002. A paper describing our preliminary results in this area has just been published.[5]

Abstract P3-5

Significant achievements: Hydrogen sorption in the nanoporous nickel phosphates VSB-1 and VSB-5 has been studied with combination of BET, temperature programmed desorption (TPD), and inelastic neutron scattering (INS) measurements. H_2 BET isotherms (Fig. 1) for VSB-1 are similar to those seen in nanoporous zeolites, while VSB-5 adsorbs substantially more hydrogen due to a steep initial uptake at low partial pressures. TPD data show that hydrogen interacts strongly with VSB-5, with desorption peaks at 109 K and 149 K in a nitrogen flow, whereas the absence of similar peaks for VSB-1 suggests a weaker interaction. INS spectra of the rotational tunnel transition of the adsorbed H_2 also reveal a strong interaction with the VSB-5 host. These data strongly suggest the existence of coordinatively unsaturated Ni^{2+} sites accessible to H_2 molecules in the pores of VSB-5. Because of their high densities (~2.8 g/ml), these VSB materials have the highest hydrogen capacities of any molecular sieve on a per volume basis.


H_2 uptake (77K) on the basis of weight

Plans for future research on this project: Specific objectives include: (i) To discover further new phases in the area of nanoporous nickel phosphates with even greater hydrogen affinity, (ii) The study of open-framework nickel materials based upon hybrid inorganic-organic moieties, (iii) To study hydrogen adsorption in mesoporous NiPOs that we have recently synthesized (unpublished results), and (iv) to seek palladium analogues of our new phases.

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(2) N. Guillou et al., Synthesis and characterization of the Ni(II) phosphate, VSB-5, a nanoporous hydroenation catalyst, Angew. Chem. 40, 2831-2834 (2001).
(3) J-S. Chang et al., Catalytic conversion of butadiene to ethylbenzene over VSB-1, Chem. Comm. 859 (2001).
(4) P. M. Forster et al., Hydrogen adsorption in nanoporous Ni(II) phosphates, J. Am. Chem. Soc. 125, 1309 (2003).

Other publications from this project in 2002-2003:

(1) C. F. Mellot et al., A combined neutron diffraction and computational study of $CFCl_3$ in NaY zeolite, Phys. Chem. Chem. Phys. (2003, in press).
(2) J. Eckert et al, Direct observation of host-guest hydrogen bonding in the zeolite NaY/chloroform system by neutron scattering. J. Amer. Chem. Soc. 124, 170 (2002).

Abstract P3-6

Advanced Fuel Cycle Initiative Support at the Radiochemical Engineering Development Center

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The Oak Ridge National Laboratory (ORNL) is participating in several areas of the Advanced Fuel Cycle Initiative Program. Three of these areas in particular are being studied at the Radiochemical Engineering Development Center (REDC) because the facilities needed to handle the radioactive materials of interest are readily available at this location. One of these areas is the group separation of the actinide and lanthanide series elements during the post-irradiation processing of the various types of reactor fuel. The objective of this work is to test selected extractants that have shown promising results for this separation, evaluating the selectivity, stability in processing schemes, resistance to radiation and chemical degradation, and required process/extractant system modifications. This effort is being carried out in the alpha glove box laboratory areas at the REDC, using diluted feed samples from the hot cell processing of highly irradiated and long-cooled plutonium targets. The second area is the continued development and demonstration of the modified direct denitration (MDD) process for various fuel processing product and waste streams. Product streams could readily be converted from a nitrate solution to an oxide product stream suitable for further use in fuel fabrication operations, and waste streams could be converted to stable oxide waste forms for storage or disposal. A rotary furnace unit is currently being installed in a glove box for use in demonstrating the conversion of plutonium and neptunium to oxide powders. The third area of interest is the demonstration of the UREX+ process in the Solvent Extraction Test Facility (SETF) in the hot cell processing area. This demonstration will also utilize feed from the ongoing hot cell processing activities with added constituents to emulate a spent reactor fuel processing feed. All of these activities utilize the unique infrastructure available at the REDC for glove box and hot cell operations and the availability of "real" processing feeds for testing these various processes.

Actinide/Lanthanide Separation Studies

A review of the literature on this subject revealed that the current work in the research community is focused on the dithiophosphinic acids and the triazinylpyridines as possible extractants for this group separation. Some of the early work in this area utilized a commercial reagent, CYANEX® 301 [bis-(2,4,4-trimethylpentyl) dithiophosphinic acid], which showed large separation factors for americium and europium with the carefully purified reagent and in synergistic systems with tributyl phosphate, trioctylphosphine oxide, and other similar compounds. However, the distribution coefficients were usefully large only at low acid concentrations (pH >3), in which high-level waste, for example, could not be treated because it would be unstable. A European study for accomplishing this separation resulted in the development of several processes under the general name, Selective Actinides Extraction (SANEX). Promising results were noted for two of the SANEX processes in particular, and the focus of the REDC work has been on these systems. The SANEX-III process utilizes a bis-triazinylpyridine compound, [2,6-Bis-(5,6-di-*n*-propyl-1,2,4-triazin-3-yl)-pyridine] and SANEX-IV utilizes a dithiophosphinic acid [bis(chlorophenyl)-dithiophosphinic acid] with aromatic substitution instead of aliphatic as in CYANEX® 301. These two reagents are not available commercially and had to be synthesized. Researchers in the Chemical Sciences Division at ORNL prepared the bis(chlorophenyl)-dithiophosphinic acid and are currently preparing the 2,6-bis-(5,6-di-*n*-propyl-1,2,4-triazin-3-yl)-pyridine. The testing with the bis(chlorophenyl)-dithiophosphinic acid extractant will be presented. Similar testing of the bis-triazinylpyridine will follow when the synthesis and purification are completed.

Modified Direct Denitration

The modified direct denitration (MDD) process is being examined for application to various streams in the processing of spent reactor fuels. In MDD, ammonium nitrate is added to a metal nitrate solution, which is decomposed directly to produce an oxide powder. MDD uses the relatively free-flowing characteristic of the decomposing double salt to produce an oxide product with the desired characteristics for use in further fuel fabrication processes. This free-flowing characteristic allows for the use of continuous production equipment such as a rotary furnace. For this study, an electrically heated rotary furnace with a 2-in.-diameter rotating tube specifically designed for use in the MDD process was procured. The associated equipment, related to off-gas handling and feed addition, has been assembled. Testing to date was done with nonradioactive surrogates, with the equipment located in a laboratory hood. These tests examined the operating conditions and equipment performance. Some modifications to the equipment resulted, and conditions that produce good operation of the kiln with the surrogate were developed. The rotary furnace is currently being installed in a glove box for testing with radioactive constituents, namely plutonium and neptunium, to determine the parameters for producing an oxide product that meets the fuel fabrication specifications. Other product or waste streams produced in the processing of spent fuels will be tested in the rotary furnace unit to determine if products with the proper characteristics for storage or waste disposal can be produced with this process.

UREX+ Process Demonstration

URanium EXtraction (UREX) is a proliferation-resistant flowsheet for chemically processing spent nuclear fuel. The primary goal of the process is to remove the uranium with sufficient purity so that it can be discarded as low-level waste. This will reduce the mass of the spent fuel by about a factor of 20 and possibly reduce the need for additional geological storage. UREX+ flowsheets will be designed to also remove plutonium, minor actinides, and Tc-99. These materials can then be destroyed in reactors via fabrication into reactor fuel or into targets for neutron activation. In the SETF, several banks of mixer-settler contactors will be used to evaluate UREX+ options. The initial tests will use a simulated feed solution containing U, Np, Pu, Am, Cm, and mixed fission products that simulates the feed from dissolving several kilograms of light-water-reactor fuel with a burnup of ~55 GW/d and 30-y cooling. The primary focus of the initial runs will be to quantitatively control the disposition of neptunium and plutonium to a desired effluent stream.

Recovery of Long-Lived Fission Products from Highly-Irradiated Pu Targets

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The nuclear properties, such as the neutron cross sections and the half-lives, of the long-lived fission product isotopes are currently of great interest. Many of these isotopes are difficult to produce in relatively large quantities by neutron irradiation because of small- to-very small neutron production cross sections. An alternative source to production by direct neutron capture is fission. The fission yields of many of these long-lived isotopes greatly exceeds what could be produced by direct neutron capture.
One of the current programs at the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL) involves the processing of highly-irradiated Pu targets for the recovery of heavy elements. This processing program offered a unique opportunity to potentially recover milligram-to-multigram quantities of long-lived fission product isotopes for research into their nuclear properties. As a result, a joint collaborative effort was established between ORNL and the Kyoto University Research Reactor Institute (KURRI).

The long-lived fission product isotopes of current interest are ^{79}Se, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{126}Sn, and ^{129}I. Gram quantities are required for neutron cross section measurements. Milligram quantities are sufficient for half-life studies. All the thermal neutron production cross sections are sub-barn in size. However, the ^{239}Pu cumulative fission product yields vary from approximately 0.04 to 6.2 atoms per 100 fissions.
The REDC is currently involved in the processing of highly irradiated, Pu targets. The design irradiation specification for these targets was 87 atom % fission, one of the highest design burnups on any DOE target. The targets were discharged in 1984 and were shipped to ORNL from SRS and PNNL in the 1990's.
The estimated yields and isotopic distributions for these long-lived fission product isotopes in a single target are given in the following table.

Table 1. Long-Lived Fission Product Isotopes As of 8/1/2002

Isotope	**Mass per target (g)**	Elemental Wt%
^{79}Se	3.083E-01	9.859E+00
^{93}Zr	3.765E+01	1.831E+01
^{99}Tc	4.798E+01	1.000E+02
^{107}Pd	4.377E+01	1.398E+01
^{126}Sn	2.370E+00	3.765E+01
^{129}I	1.044E+01	6.617E+01

The flowsheet used to process the highly irradiated Pu targets uses a caustic-nitrate dissolution of the Al housing and matrix material followed by a nitric acid dissolution of the actinides and rare earth fission products. The PUREX method is used to recover the Pu. Batch extractions on the PUREX aqueous phase with HDEHP and acid strips (the CLEANEX process) are used to recover and purify the Am and Cm.

The effort is currently focused on analyzing the streams in the CLEANEX process for the long-lived fission product isotopes. In the CLEANEX process the acid phase of PUREX is batch-contacted with 1 M HDEHP in order to purify the Am/Cm/Rare earth fission products from any residual Pu and other fission products. The HDEHP organic phase is contacted again with 5 M HNO_3 in order to strip any transplutonium elements that were extracted into the HDEHP phase. Using ICP-MS, ^{99}Tc and ^{107}Pd were found in the first HNO_3 extraction raffinate. Fission product Zr was assumed to follow "tramp" Pu in the first HDEHP organic stream of the CLEANEX process. Samples were taken from the organic stream and were stripped with a variety of solutions. Zr-93 was identified using ICP-MS. No ^{79}Se or ^{129}I was found in the raffinates or the extractions. The assumption is that the ^{129}I is in the caustic-nitrate solution or the caustic dissolver off-gas system. The Se may be distributed over several processing streams. However, its low yield and large solution volumes makes measurement difficult. Sn-126 was not included in the early analyses.

A number of strip solutions were investigated for Zr stripping efficiency. One of the strip solutions was 0.6 M oxalic acid. A full-scale oxalic acid strip was made on the CLEANEX HDEHP process stream from 3/8 of a target. The oxalic acid strip was contacted with concentrated HNO_3 and reduced in volume. The fission product Zr precipitated out of solution, most likely as an oxalate.

Initial efforts to dissolve the precipitates with H_2SO_4 were discouraging. HF-dissolution of the precipitates was much more successful. However, the use of these two acids on a large scale is discouraged because of corrosion issues. As a result, some "cold" tests have been made using NaOH to convert the Zr oxalate to the hydroxide form with subsequent dissolution in 9 M HCl or 10 M HNO_3. These "cold" tests show some promise and there are plans to conduct these conversions on "hot" samples.

ICP-MS analysis did reveal the presence of ^{99}Tc and ^{107}Pd in the extraction raffinate from the CLEANEX process. An effort has been initiated to develop a ^{107}Pd recovery method. In "cold" tests, the addition of ascorbic acid has reduced the Pd ions in the nitric acid solution to Pd metal precipitates. Ascorbic acid was also added to small samples of the CLEANEX extraction raffinate from the most recent transplutonium target processing campaign. The small samples immediately changed color and maintained the color change for many hours, presumably due to precipitation of fission product Pd. However, within 24 hours of the addition of the ascorbic acid the color disappeared indicating the Pd may have gone back into solution. Tests are continuing in order to see if this is a viable method for recovering fission product Pd.

Efforts have also been initiated in order to determine the presence of Se in the various processing streams and in developing a procedure for recovering fission product Tc from the first CLEANEX extraction raffinate. No work has been done to-date on examining the caustic-nitrate solutions or the caustic dissolver off-gas system for the presence of the fission products of interest.

The Savannah River MK 18A Target Assemblies: A National Resource of Pu and Cm

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The Savannah River MK 18A target assemblies were irradiated by DOE–Savannah River to produce multi-gram quantities of ^{252}Cf for the Cf-252 Market Program. These targets were charged with ^{242}Pu and were exposed to the highest thermal neutron flux of any targets in the DOE complex. The Cf-252 Market Program never required the quantities produced in the MK 18A target assemblies. As a result, the targets have been in storage at the Savannah River Site and the ^{252}Cf has decayed to small quantities. The target assemblies do contain, though, the world's largest remaining supply of ^{244}Pu and heavy Cm isotopes. Both ^{244}Pu and heavy Cm isotopes are extremely hard to produce and the capabilities to produce these quantities no longer exist.

Pu-244, the longest-lived of all the Pu isotopes, has a multitude of uses. These include safeguards applications, Pu detection in environmental samples, forensic studies in the detection of diversion activities and covert production and processing, measurement of declared reactor fluxes and nuclear physics and chemistry research and development. The heavy Cm isotopes are excellent feed material for both isotope separation for nuclear physics and chemistry research and development and for the production of heavier isotopes and elements.

Much effort has been undertaken to preserve the target assemblies. This includes solving a number of technical challenges in handling and transportation. Disposition paths have been identified and analyzed. Funding to recover and process the MK 18A target assemblies has not been found, though.

The MK 18A irradiation program at the DOE-Savannah River Site (SRS) was initiated to produce multi-gram quantities of ^{252}Cf. Eighty six MK18A target assemblies were charged to K reactor in late 1969. The reactor operated in a high thermal flux mode ($>2 \times 10^{15}$ n/cm^2-s) for the first 14 months with typical fuel cycle lengths of 4 to 5 days with 1 day downtime. The last 9 years of irradiation were at much lower neutron fluxes and ended in 1979. Twenty one target assemblies were sent to Oak Ridge National Laboratory (ORNL) in the early 1970s for processing in support of the Cf-252 Market Program. Pu-244 was also recovered from these assemblies and some of it was enriched in the ORNL Calutrons. This isotopic separation provided the supply of enriched ^{244}Pu in use today. Sixty-five MK 18A target assemblies remain in storage at SRS. The MK 18A target assemblies were declared a "national resource" by DOE in 2000.

The quantities of actinides in the MK 18A target assemblies are shown in Tables 1 and 2. Pu-244 is extremely hard to produce, primarily due to the short half-life of its ^{243}Pu precursor ($t_{1/2}$ = 4.956 hrs). Production of useable quantities requires a very high thermal flux typical of what K reactor produced. For this reason, ^{244}Pu is virtually non-existent in reactor fuel or weapons-grade Pu. This non-existence of ^{244}Pu in these types of Pu makes it a valuable analytical tracer.

Table 1. Actinide Inventory in MK 18A Target Assemblies

Element	Mass (g)
Total Pu	344.2
Total Am	30.3
Total Cm	665.2
Total Cf	0.61
Total	1040

Table 2. MK 18A Pu Isotopics

Isotope	Mass (g)	Wt%
^{238}Pu	0.18	0.05
^{239}Pu	0.04	0.01
^{240}Pu	288.20	83.73
^{241}Pu	6.04	1.75
^{242}Pu	30.60	8.90
^{244}Pu	19.10	5.55
Total (1/1/2002)	344.2	

The most frequent use of ^{244}Pu is as a spike in isotope dilution mass spectroscopy (IDMS). The use of ^{244}Pu allows for precise quantitative determination of all the Pu isotopes in the IDMS sample. Very high isotopic purity ^{244}Pu provides for Pu detection at a 1000-fold higher sensitivity than the most sophisticated counting techniques. The use of ^{244}Pu also allows for accurate measurement of the minor Pu isotopic ratios, thus permitting the determination of past histories. It also makes feasible quantitative Pu analysis on ultra-small Pu samples with a single spike. It also permits a greater range of spike-to-sample ratios with a greater accuracy than other Pu isotopic spikes.

Pu-244 also finds very valuable applications in nuclear chemistry and physics research and development. Pu-244 is used as a target for the production of superheavy elements and the study of reaction mechanisms. It has been used in double beta decay experiments, as target material for the production of ^{247}Pu and as a source for ^{240}U. The use of ^{244}Pu in metallurgical and chemical research and development would minimize radiolytic effects and allow for a better understanding of the fundamental chemistry.

Pu-244 might also assist in understanding the aging issues related to stockpile stewardship.

The physical and radiation properties of the MK 18A target assemblies present a number of technical challenges. In addition, the conversion of SRS to a DOE-EM site and the capacity of the SRS canyons makes processing and recovery at SRS problematical. However, transportation to the REDC and processing of the targets at the REDC are feasible with little modification. No funding agencies have been identified yet.

Abstract P3-9

Neutron Sources for Cancer Therapy and Other Research at the Californium User Facility for Neutron Science

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Overall research goals

1. *Design and fabricate ^{252}Cf neutron sources for cancer treatment* that are significantly smaller but more intense than sources previously fabricated within the U.S., for use in treating brain and other tumors resistant to conventional radiotherapy.

2. *Utilize ORNL's Californium User Facility for Neutron Science (CUF) to promote nuclear and multidisciplinary research in the applications of neutrons.* The CUF specializes in medium-flux fast neutron irradiations (fluxes ~10^9 cm^{-2} s^{-1} and fluences $\leq 10^{14}$ cm^{-2}).

Background

A single compact, sealed ^{252}Cf source can emit up to 10^{11} neutrons/s. These sources are ideal for industrial and research applications[1,2] requiring medium-flux neutron irradiations, such as neutron activation analysis,[3] neutron radiography, irradiation damage testing of permanent magnets[4,5] and solid-state detectors, and neutron-induced mutation of seeds.[6] However, this source geometry is too large for optimized brachytherapy treatment of cancer, in which a small radioactive source is inserted through a catheter (plastic tubing) to the tumor location inside the patient's body, to irradiate and kill the cancer cells.[7,8,9] In 1999 ORNL teamed with Isotron, Inc., of Alpharetta, Georgia to develop miniature ^{252}Cf medical sources for optimal treatment of virulent brain tumors, as well as gynecological and prostate tumors, tumors of the head, neck, and oral cavity, and locally advanced breast cancer.

Specific objectives for 2002–2003

1. *Demonstrate a Cf-containing wire source form that is significantly thinner than any previously available from ORNL.*

2. *Demonstrate the complete fabrication process for prototype ^{252}Cf medical sources,* designed around this new, thinner source form.

3. *Calibrate a neutron detector used to monitor the ambient background of photoneutrons in Argonne's Advanced Photon Source (APS),* using both fast and thermalized neutrons.

4. *Design, fabricate, and demonstrate an irradiator module to provide a thermalized low-flux beam of neutrons* for testing neutron detectors to be used in ORNL's Spallation Neutron Source (SNS), currently under construction.

Significant achievements

1. *Fabrication of high-intensity ^{252}Cf cermet wires significantly thinner than any previously fabricated under DOE's Californium Industrial Sales Program .* The source form consists of a cermet wire containing ~1% by weight of ^{252}Cf (as Cf_2O_3) in a palladium matrix.

2. *Design, assembly, and demonstration of almost all hardware and handling components required for the fabrication and delivery of miniature ^{252}Cf medical sources, followed by fabrication of the first higher-intensity medical source prototypes of a size comparable to*

existing gamma brachytherapy sources.[7,8,9] This miniaturized source enables use of existing medical accessories for treatment. Even with the smaller size, the neutron intensity was increased several-fold over previous U.S. ^{252}Cf brachytherapy sources.

3. *Characterization of APS neutron detector response to 2.5-mg ^{252}Cf source.* The response of an LND, Inc., model 30763 fission counter was determined for several source-to-detector distances, and the neutron flux and energy spectrum at the detector characterized by MCNP-4C calculations and gold foil activation. Data are currently under analysis.

4. *Design of a low-flux ^{252}Cf neutron irradiator,* currently under construction, to provide future testing of neutron detectors for ORNL's SNS. This irradiator is based on ~30 μg of ^{252}Cf inside a commercial shipping container, which is fitted with an MCNP-designed polyethylene hat to provide a horizontal neutron beam with thermal flux >100 cm^{-2} s^{-1}. This irradiator will be available in 2003 for testing detectors and other samples and for educational purposes.

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Abstract P3-10

Plutonium-238 Production Support Studies

(conducted by REDC staff)

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The Department of Energy (DOE) supplies Plutonium-238 (^{238}Pu) to NASA as an enabling power supply for deep space missions. Currently, the United States does not have a domestic source of ^{238}Pu. The Radiochemical Engineering Development Center (REDC) has been conducting radiochemical processing operations for the DOE in support of the DOE Heavy Element Program. The DOE supplies REDC heavy actinides to researchers throughout the DOE complex for basic research on the chemistry and physics of these isotopes. Recently, the Department evaluated potential sites which could be put into service to resume ^{238}Pu production. The REDC Building 7930 was chosen as the target fabrication and chemical processing site. REDC developed flowsheets for plutonium purification and neptunium recovery based on experience gained in the Heavy Element Program. Previous research efforts have included target design, target irradiation, and post irradiation examination of selected targets. Current efforts have focused on transferring nuclear material from the Savannah River Site to Oak Ridge National Laboratory. The production of the ^{238} Pu requires long-term storage of the feedstock ^{237} Np. As in other long-term actinide storage programs, there is considerable controversy concerning gas generation over long periods of time. Experiments were conducted to mock up long-term storage conditions. Recent results from gas generation studies will be described.

Abstract P3-11

Heterogeneity and Collective Phenomena in Crystalline Solids

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Overall research goals

The global objective of this project is to elucidate the origins and implications of the identification by local structure measurements of heterogeneous, differently structured domains embedded in the host lattice of materials that are homogeneous when analyzed by conventional crystallographic methods. Materials exhibiting these characteristics are typically termed "complex," display correlated electronic (superconductivity, magnetism, etc.) and atomic (transformational) properties, and usually have compositions that do not correspond to the stoichiometry of their unit cells. Insofar as many of their compelling properties are at best only poorly understood, nanoscale heterogeneity may provide critical insights into their structure:property relationships. This work will involve a combined experimental-theoretical approach. Experimental studies will be pursued on many systems to characterize the various forms in which local lattice distortions and collective behavior occur. Parallel theoretical development will attempt to develop methods for predicting the structures and properties of "real" materials and move away from the periodic, mean field approaches that have dominated the study of condensed matter.

A second objective is to support additional determinations of local structure and chemical speciation of actinide-containing systems using synchrotron x-ray techniques.

Specific objectives for 2002-2003

Complete analysis and interpretation of fcc-bcc transition in Fe thin films. These results indicated that the anomaly in the distorted fcc region was most likely caused by a large increase in the

Fe-Fe distance in the c direction only at the interface, with the low symmetry consistent with the magnetic behavior.

Analysis and interpretation of the anomalous pdf results on UNb was completed. These show some evidence of non-crystallographic, longer range Nb-Nb interactions, indicative of cooperativity between the Nb sites that earlier XAFS measurements had demonstrated had radically different environments that the U despite being a solid solution.

Obtain new XAFS measurements on a cuprate superconductor and analyze in terms of the extended polaron indicated by the Egami mode.

Perform XAFS measurements on UO_{2+x} for comparison with earlier PuO_{2+x} experiments showing the excess O occurs as Pu(V) oxo groups.

Complete analysis of shocked Zr data, the bcc phase of which shows a structural modulation very similar to that observed in the sigma structure of Pu alloys.

Significant achievements

The most significant achievements over the last year occurred in the theory development area. A series of structure factor calculations have demonstrated several ways in which heterogeneous, ordered, nanophase separated arrangements of atoms can be crafted with minimal or negligible effects on diffraction patterns, which was a critical element of this proposal. After two years of struggling with a rules-based algorithm for determining atom positions in solid solutions, a switch was made to an energy minimization code using force constants designed to duplicate the experimental features of the local environments. Success occurred quickly with this novel approach, and it has already been used to demonstrate that deviations from Vegard's Law can result from changes in the extent of cooperativity involved in locating the solute atom positions in the lattice. We have also now been able to use the FEFF code to perform cluster calculations through a heterogeneous structure to identify aspects of the local electronic structure. Our first rigorous example has been to apply this to the antiferromagnetism in disordered NiMn spin-glass, where it indicates that the spin ordering in the AFM L_{10} domains remains fully developed except for a narrow region at the interfaces. This is consistent with our earlier experimental measurements and is consistent with the properties of magnetic materials originating in local properties instead of homogeneous, mean-field behavior.

A second achievement was organizing the conference Local and Nanoscale Structure in Complex Systems. This conference was designed to explore full range of systems in which the properties of interest are coupled to multiple, coexisting conformations, including alloys, correlated materials, biomolecules, catalysts, soft matter, and fabricated heterostructures. It was attended by approximately 120 scientists from North America, Asia, Europe, and Australia, including Neal Ashcroft, James Krumhansl, and Walter Kohn.

Plans for future research on this project:

The most important future goals are to:

- is to explore the origin of nanoscale heterogeneity by incorporating a double well potential that can be coupled to the local environment and entropy;
- Continue local electronic cluster calculations, emphasizing structure:property relationships;
- Extend integrated cluster type approaches to phonons and other properties.
- Continue experimental work.

Abstract P3-12

Hybridization, delocalization, and disorder effects in *f*-electron intermetallics

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Overall research goals: Hybridization between *f* electrons and conduction electrons in intermetallic compounds gives rise to a variety of magnetic ground states. These states are generated by the competing Ruderman-Kasuya-Kittel-Yosida (RKKY) and Kondo interactions, the former generally giving rise to magnetic states, such as a ferromagnet, and the latter to non-magnetic states. When lattice disorder is convolved into these interactions, one needs to consider the following phase diagram:

	Disorder→	
Hybridization↓	**RKKY** ferromagnets, anti-ferromagnets	Spin glasses
	NFL's?	
	Kondo single impurity, Anderson lattices	Non-Fermi liquids

When these interactions are the same strength, a new and poorly understood state develops with properties (especially magnetic) that contrast sharply with the Fermi liquid (FL) theory thought to apply to these systems. Many of these non-Fermi liquid (NFL) properties are shared by the high-temperature superconductors, with the advantage that the magnetic properties of the ground states are more accessible in the *f*-electron intermetallics due to the absence of a (strong) Meissner effect. The *f*-electron intermetallic NFL's are therefore a fertile ground for exploring NFL physics. Since most known NFL materials have some form of lattice disorder, it is important to develop theories that include lattice disorder and to test real materials experimentally for lattice disorder. In addition, even the theory of the Kondo interaction in a concentrated system of magnetic ions (a.k.a. the Anderson lattice) remains unsolved. Therefore, we are exploring the above phase diagram from the perspective of the effect of lattice disorder on each type of system. Our studies utilize x-ray absorption spectroscopy techniques as a unique probe of the local electronic and atomic structure around the *f*-ions.

Significant achievements. By studying a large subset of the $UCu_{5-x}Pd_x$ series, we have differentiated between bond length disorder around the uranium atoms (as predicted by one theory) and Pd/Cu site interchange.[1] Although this system is chemically disordered, the bond length disorder is insufficient to generate NFL behavior by conventional means. However, we know that lattice disorder plays a role, since annealing samples of UCu_4Pd produces changes in the NFL properties. Our studies[2] show directly what changes occur in the lattice. Although the lattice disorder model cannot easily account for all the NFL properties in this material, *changes* in the lattice disorder can account for changes in these properties. We have also completed a study of the $U_3Ni_3Sn_4$ NFL system[3] and shown that by all measures, this material is stoichiometric and well ordered. Moreover, we have performed magnetic-field dependent heat capacity measurements that, together with the structural data, rule out all current disorder NFL models. This research thus indicates that $U_3Ni_3Sn_4$ is a leading candidate for a true, ordered, NFL system. Studies on the Anderson lattice $YbAl_3$ system[4] will also be presented.

Specific objectives for 2002-2003: As grown samples of URh_2Ge_2 display canonical spin glass properties, but annealing generates anti-ferromagnets, indicating that the magnetic-interaction disorder in the anti-ferromagnets in on the cusp of being sufficient to generate the spin glass state. A continuing problem has been determining the dominant crystal phase, and therefore the form of the lattice disorder that generates the spin glass phase. Analysis of XAFS data should determine the nature of the most likely dominant phase, and may indicate what the structural differences are between the spin glass and anti-ferromagnetic samples. We have also embarked on a study of the $Yb_{1-x}Lu_xAl_3$ system to study the development of the Anderson lattice from the single impurity limit. Measurements include Yb XANES for determining the *f*- hole content as a function of temperature, as well as magnetic susceptibility (up to 800 K due to the high temperature scale of the Kondo state), Hall effect and other properties.

Plans for future research of this project: All of the principal research areas in the phase diagram (apart fro the pure magnetic phases) remain understudied. In addition to looking at more NFL materials such as UCoAl with our standard probes, we will soon begin to perform XANES measurements under applied pressure at the High Pressure CAT at the Advanced Photon Source. In addition, we will begin to feature research on the Ce-115's, such as the NFL $CeCoIn_5$ system, and possibly the superconducting $PuCoGa_5$ system.

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Abstract P3-13

Pressure-induced changes in actinides: Importance for understanding actinide bonding.

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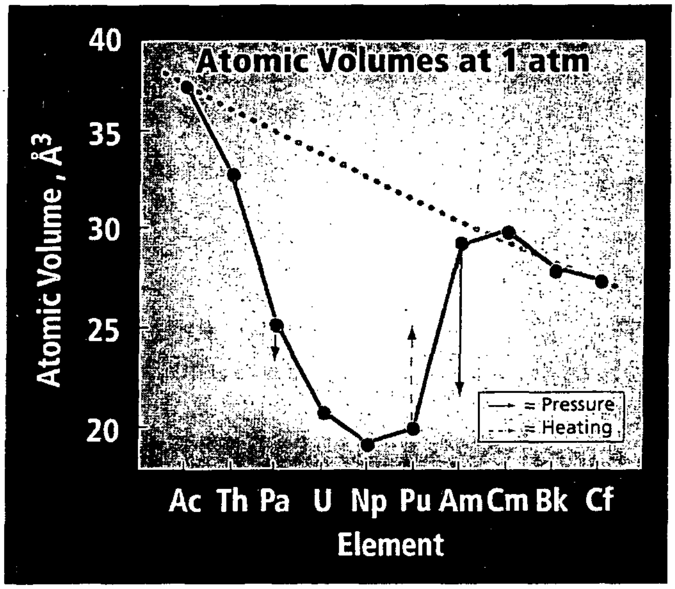
Introduction and Goals:

The overall research goal of our investigations is to examine the effect of decreasing interatomic distances brought about by pressure on the metallic bonding of actinide metals, alloys and compounds. A specific aspect here is the incorporation of f-electron character into the bonding by pressure; where the latter is normally present in the protactinium through plutonium metals at atmospheric pressure. Acquiring experimental data for this process will provide an improved understanding of the bonding and electronic nature of these materials, and generate important systematics for the f-elements. The experimental data will also provide a platform to evaluate and fine tune theoretical predictions for and the understanding of these elements.

Important changes in the role of the 5f-electrons can be extracted from perturbations encountered in their atomic volumes and structures. This is represented for the volumes of selected elements shown in the figure. The dotted curve suggests the volumes expected if only localized 5f-electrons were present in the bonding, whereas the smaller volumes for the Pa through Pu elements reflect the presence of itinerant 5f-electrons and greater degree of bonding. The arrows in the figure depict changes in selected metals arising from the application of pressure (americium and protactinium) or temperature (plutonium).



Significant achievements in this scientific arena have been acquired in international collaborative studies, both with americium[1] and very recently with protactinium[2] under pressure. The earlier work on americium established that pressure forced a step-wise increase in the 5f electron character of its bonding, with the metal first acquiring a gamma-plutonium structure and then an orthorhombic structure (retained to 100 GPa) which is very similar to that for alpha-uranium.

Significant Recent Achievements:

Similar studies have been performed very recently on protactinium metal[3], the first element to normally posse itinerant 5f-electron character at atmospheric pressure. It was determined in experimental studies with synchrotron radiation (ESRF, Grenoble, France) up to 130 GPa, that its tetragonal structure (space group, I4/mmm) converts to an orthorhombic, alpha-uranium structure (space group, Cmcm) at 77(5) GPa, with only a small (0.8%) change in relative volume accompanying the transition. This second structure was retained up to 130 GPa. This structural change is interpreted as reflecting a small, pressure-induced increase in the 5f-electron contribution to protactinium's bonding. Extrapolating the compression curves of the high-pressure phases of americium and protactinium back to one atmosphere suggests pseudo-atomic volumes that would exist for these structural forms, if retained at one atmosphere. This is represented by the small downward arrows in the figure. The small change for protactinium suggests only a slight increase in bonding, but sufficient to generate an alpha-uranium structure.

Future Plans:

Future research in this area is planned to address the behaviors of curium and californium metals under pressure. When progressing across the actinide series the 5f-electrons are "pulled-in," and it is expected that higher pressures will be needed to achieve any itinerant, 5f-electron behavior. Another goal will be to determine if these metals will also form "standard" pressure structures after acquiring varying degrees of f-electron involvement in their bonding. Additional efforts will examine other actinide alloys and metals (studies on an $Am_{0.5}Cm_{0.5}$ alloy[3] and other metals[4] under pressure have been reported recently). With alloys, one can look at the changes for materials representing a "fractional change "in atomic number. Work on other actinide compounds under pressure will also be pursued; we recently reported on the behavior of americium and curium dioxides under pressure[5].

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Abstract P4-1

Soft X-ray Synchrotron Radiation Investigations of Actinides and the Advanced Light Source Molecular Environmental Science Beamline

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Overall research goals:

Synchrotron radiation (SR) methods have been utilized with increasing frequency over the past several years to investigate fundamental actinide science. The actinide research community has capitalized on SR methodologies for investigations of radioactive materials because of improved radiological safety infrastructure, improvements in detector technologies,[1] and the capability to perform experiments with small amounts of actinide material. In particular, the emergence of microspectroscopic and fluorescence-based techniques have enabled investigations of actinide materials at sources of soft x-ray SR.

One focus of the actinide research program is on elucidating and understanding the roles of the 5f electrons in the chemical bonding of the actinides; characterization of the electronic structures of actinide materials; surface chemistry of actinide materials; and the optimization of soft x-ray SR techniques for actinide investigations. The successful construction of the Advanced Light Source Molecular Environmental Science (ALS-MES) Beamline has enabled the final stage of beamline development to establish a unique, innovative, and productive experimental facility for soft x-ray SR users.

Specific objectives for 2002-2003:

An immediate objective is to maintain the momentum gained from successful soft x-ray SR investigations of actinides at the ALS and to extend these experiments to systems with heavier actinides. Of paramount importance is ensuring the timely, successful installation of user scientific programs at the ALS-MES Beamline and the continued development of Beamline capabilities. Two new collaborative efforts will be initiated. The first will be with K. Raymond on actinide coordination/complexation and the second with T. Gouder on the preparation of actinide thin films followed by SR photoelectron spectroscopy at the ALS.

Significant achievements:

The photon-in, photon-out techniques of x-ray emission spectroscopy (XES) and resonant inelastic x-ray scattering (RIXS) investigations of actinides continue to progress with soft x-ray SR. The results from a polarized RIXS study of UO_3 were communicated and show that the 9.5 eV loss feature is attributable to an oxygen 2p-uranium 5f charge transfer satellite.[2] The feature is difficult to identify without the polarization measurements. The first data from thorium boron materials (ThB_2 and a ThB_2/ThB_4 mixture) and thorium references were collected using the XES spectrometer at Beamline 8. This follows closely on similar work recently conducted with uranium borides. A complete set of RIXS spectroscopic data was collected from iron surfaces exposed to low concentrations of uranyl. The first use of liquid cells with an actinide was also successfully demonstrated in the soft x-rays with a uranyl solution.

The soft x-ray photoelectron spectroscopy efforts at the ALS continue and the development plan for an actinide end station has been described in a recent communication. The construction of the actinide end station has been nearly completed, although modifications are being made to permit spin-polarized electron detection and to improve the functionality with actinide materials.[4]

The construction of ALS-MES Beamline 11.0.2 at LBNL has recently been completed. The ALS-MES Beamline is the first, soft x-ray SR beamline designed for and dedicated to MES investigations. The 5.0 cm period elliptically polarized undulator (EPU) beamline provides monochromatized SR from 75 eV to 2000 eV with controlled polarization downstream from a newly-designed LBNL variable-angle-included-plane-grating monochromator. The beamline has two branchlines, one dedicated to surface science-style spectroscopy end stations and the second to scanning transmission x-ray microscopy. The overall beamline design incorporates features for beam stability, high resolution, high flux, and ease of user operation.

Plans for future research:

The scientific research directions in the actinide chemistry soft x-ray SR program will continue to build on recent developments and will make use of the unique characteristics of soft x-ray SR beamlines for actinide experiments. The focus of the soft x-ray SR actinide research investigations will remain on the roles of the 5f electrons in chemical bonding, characterization of electronic structures, and the surface chemistry of actinide materials. An actinide materials preparation capability will be developed around a compartmentalized, commercially-modified, inert-atmosphere radiochemical glove box. This will be used to prepare purposefully engineered novel actinide materials and actinide interfacial systems.

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M. Karabulut, G. K. Marasinghe, C. S. Ray, D. E. Day, G. D. Waddill, P. G. Allen, C. H. Booth, J. J. Bucher, D. L. Caulder, N. M. Edelstein, and D. K. Shuh, "Investigation of the Local Iron Environment in Iron Phosphate Glasses with Different Fe(II) Concentrations," J. Non-Cryst. Solids **306**, 182 (2002).

Abstract P4-2

Micellar Surface Structures

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Overall Research Goals: The basis of particle separations by froth flotation is the hydrophobic surface state. This state can be selectively created at the surface of specific particles using appropriate surfactants and separation of hydrophobic particles is achieved by attachment to air bubbles. Understanding and control of the hydrophobic surface state, important in many areas of technology, is the general quest of our research program which includes,

- Study of the interfacial water structure by vibrational spectroscopy,
- Interaction force measurements using the AFM colloidal probe technique, and
- Characterization of adsorbed surfactant layers by surface spectroscopy and AFM imaging.

In this way it is intended to provide a fundamental surface chemistry foundation for improved particle separation technology by froth flotation.

Specific Objectives for 2002-2003: One particular aspect of our research objectives, the study of surfactant surface structures, is discussed in this presentation. The effects of surfactant headgroup and cosurfactant addition on micellar surface structures are reported. Dodecyl amine surfactants were used to study the effect of surfactant headgroup at both hydrophobic graphite and hydrophilic mica surfaces. To study the effect of a cosurfactant, the changes brought about in sodium dodecyl sulfate (SDS) micellar surface structures at graphite surfaces were examined from the addition of the nonionic dodecanol and the cationic dodecyl trimethyl ammonium bromide (DTAB).

Significant Achievements: At the graphite surface, changes in the surfactant headgroup did not cause any significant changes in the surfactant structures. Identical well organized linear hemicylindrical structures were observed for primary, tertiary and quaternary ammonium surfactants, as shown for dodecyl amine in Figure 1. The only difference observed was in the spacing of those hemicylinders which increased from 3.8 nm for primary to 5.6 nm for quaternary amines. Details of the micellar surface structures are depicted in Figure 2. In contrast, significant shape transitions were observed for these surfactants at a hydrophilic mica surface

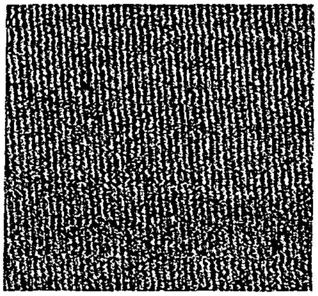


Figure 1. 200 nm AFM image of dodecyl amine at a graphite surface, natural pH, spacing 3.8 nm.

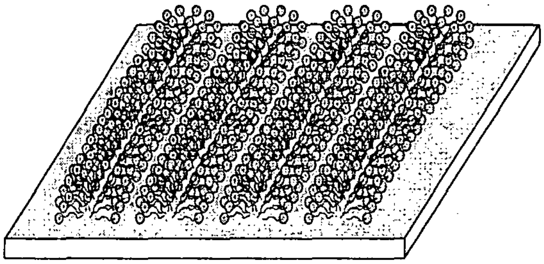
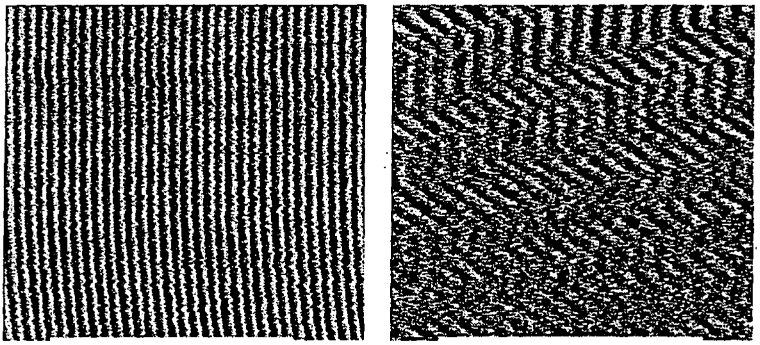


Figure 2. Schematic showing the highly ordered hemicylindrical micellar strucutres at a graphite surface.

going from primary to tertiary to quaternary amines. No structures were observed for the primary amines, cylindrical like structures were observed for the tertiary amines, and spherical structures were observed for the quaternary amines [1]. This behavior is in good agreement with the shape transitions in bulk micelles from primary to quaternary amines.

In general, the addition of a cosurfactant to the surfactant solution increases the relaxation times of micelles in bulk solution. At graphite surfaces, the cosurfactant effect is manifested in the form of changes in the adsorbed structures at the surface and the kinetics of adsorption. Inducing the additional ion-dipole or ion-ion interactions through the addition of dodecanol or DTAB respectively, caused significant changes in the otherwise highly ordered linear hemicylindrical SDS surfactant structures at the graphite surface as shown in Figure 3. It is evident that the linear hemicylindrical micellar structure is interrupted but a herring-bone pattern is preserved with macro periodicity. Further the diameter of the micellar structures increases from around 5 nm to 8 nm. Evidently significant swelling occurs. The adsorption kinetics also varied significantly [2].



Spacing ~5 nm

Spacing ~8 nm

Figure 3. 200 nm AFM images of 100 mM SDS (left), spacing ~ 5nm, and 100 mM SDS + 5 mM dodecanol (right) surfactant structures, spacing ~ 8nm, at graphite surface.

These micellar surface structures are considered with respect to FTIR/ATR spectroscopic measurements, streaming potential measurements, and theoretical considerations.

Plans for Future Research on This Project: Research continues on the study of these surfactant surface structures to compliment other research activities involving SFG spectroscopy and AFM interaction force measurements. Other more applied research includes the development of flotation technology for trona and phosphate mineral resources.

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Other Publications from This Project in 2002-2003: Several other papers from this project were published/submitted in several scientific journals (J. Colloid Interface Sci., Langmuir, Minerals Eng., Int. J. Miner. Proc., Physchem. Problems Miner. Proc., Colloids Surfaces) during 2002-2003.

Principles of Chemical Recognition and Transport in Extractive Separations: Molecular Modeling and Host Design

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Overall research goals: Ion-recognition through discovery and exploitation of host-guest principles in extractive separations constitutes the primary objective of this research. The core question addresses how the structure of host molecules governs their ability to recognize ionic species and effect selective, efficient separations as modulated by matrix interactions. A major focus is the deliberate design of receptors for anions, both to learn how to enhance salt extraction and to understand factors determining anion selectivity. Representing the theoretical component of the multi-disciplinary team led by Bruce Moyer at Oak Ridge National Laboratory, our research centers on the use of molecular modeling to address fundamental questions concerning the design of superior extractants and resins for chemical separations in support of environmental and other needs of the USDOE. The theoretical objectives are (1) to develop sufficient structural criteria to allow the deliberate design of candidate host structures with maximum organization for coordination to targeted ionic species and (2) to generalize the design process computationally. Ultimately, we hope to design molecular architectures in which anion– and cation–receptor functions are combined into a single ditopic host for the recognition of complete ion pairs.

Specific objectives for 2002-2003: Current research centers on the computational design of anion host molecules constructed by assembling hydrogen–bonding components to obtain complementary and preorganized architectures. One objective is to derive a set of structural design criteria for hydrogen–bonding interactions between oxyanions and various donor groups. Such criteria will be based on examination of crystal-structure data and the results of electronic-structure calculations. A second objective is to bring the *de novo* structure–based design approach to supramolecular chemistry by learning how best to generalize the computations. A final objective is the application of computational design methods to identify candidate host architectures for synthesis and testing.

Significant achievements: The deliberate design of ion receptors requires the capability to distinguish hosts that efficiently complement guest ions. Accurate electronic-structure calculations can be coupled with experimental data to provide fundamental knowledge about host structure and the nature of ion—binding site interactions. Such studies, now in progress, have yielded several new insights. Examination of hydrogen bonds in crystal structures reveals a distinct and general directionality for the oxygen atom acceptors of trigonal planar and tetrahedral oxyanions.[1] Optimized geometries obtained from electronic–structure calculations on one–to–one hydrogen–bonded complexes between oxyanions, such as nitrate and sulfate, and various unidentate donor groups exhibit structural features that are consistent with those observed in the solid state.[2]

The ability to evaluate potential host structures is only half of the design process. The other half is coming up with the set of host structures to be evaluated. To bring the powerful concepts employed in structure-based drug design to bear on host design, we have devised novel algorithms for building potential host structures from molecular fragments and rapid methods for prioritizing the complementarity of the resulting candidates for a targeted ion guest. The algorithms are embodied in a new computer software program, called HostDesigner, which can generate and evaluate millions of new molecular structures per minute on a desktop personal computer.[3,4] This software is available at no cost to the scientific community and can be downloaded from the HostDesigner website: http://hostdesigner.emsl.pnl.gov.

Plans for future research on this project: Future efforts will focus on the deliberate design of anion receptors based on bidentate hydrogen–bonding components such as guanidinium and amidinium cations, and urea. Information gained from electronic–structure calculations will be used in the design of potential host architectures composed of two or three bidentate components, providing both input for HostDesigner and a basis for the derivation of molecular mechanics models needed to score potential candidates. Synthesis and evaluation of designed structures, performed by collaborators at ORNL, will provide valuable structure-function data needed to test the validity of the theoretical approach.

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Abstract P4-4

Fundamentals Of Electric Field-Enhanced Multiphase Separations And Analysis

(DE-FG02-96ER14641 A8)

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The problem of the dynamics and formation of drops in the absence as well as the presence of electric fields is of great interest because of its prevalence in applications and the richness of the underlying science (see the review article by Basaran 2002). In applications as diverse as separations, ink jet printing, DNA and protein arraying, deposition of reagents on diagnostic test strips, and manufacture of particles and microcapsules, the formation of drops from nozzles plays a central role. Scientifically, analysis of drop formation requires solution of a tough free boundary problem that exhibits occurrence of finite time singularities. Therefore, a major objective of this research program is to study through theoretical, computational, and experimental means the physics of interface rupture in single-fluid, e.g. a drop forming in air, and two-fluid, e.g. a drop forming in another liquid, systems in the absence and presence of electric fields. A long-term goal of this research is to exploit the fundamental understanding gained through the aforementioned studies to improve the efficiency of electroseparations and advance the science of microencapsulation processes among others.

A major focus area of research has been analysis of pinch-off and scaling behavior during interface rupture. Chen et al. (2002) have used high-accuracy computation and ultrafast, high-resolution imaging to study breakup of *drops of Newtonian liquids in air.* In this study, the interface of a water drop ($\mu \approx 1$ cp) has been shown to overturn prior to breakup for the first time in an experiment, well before the dynamics transitions from the potential flow (PF) to the inertial-viscous (IV) regime. Furthermore, this study has also shown that a drop of 83% glycerol-water solution ($\mu \approx 85$ cp) exhibits a transition from the PF to the IV regime both experimentally and computationally. Moreover, Chen et al. (2002) have also shown that the computed value of the minimum neck radius in the latter case follows Eggers's universal solution. This study has demonstrated that the computational algorithms developed in this research program have unparalleled accuracy in that their predictions quantitatively accord with both experiments and scaling theories. More recently, we have started to analyze the pinch-off of *drops of complex fluids in air.* Doshi et al. (2003) have carried out an asymptotic analysis to determine scaling exponents and self-similar solutions governing the pinch-off of drops of generalized Newtonian fluids in air.

Another major focus area has been development of accurate and efficient computational algorithms for solving free boundary problems with interface rupture. This research program addresses the development of algorithms that solve the full set of two- or three-dimensional equations (Chen et al. 2002, Notz and Basaran 2002) and highly accurate but reduced set of equations based on the slender-jet approximation. We have recently evaluated for the first time the accuracy of such approximations (Ambravaneswaran et al. 2002). Work is underway to extend such algorithms and comparisons to situations in the presence of surfactants (Liao et al. 2003a,b).

Yet another focus area has been development of novel methods for production of microscopic droplets.. We have used high-accuracy computation and ultra high-speed imaging (at rates of 100 million frames/sec) in order to uncover these new means of drop generation. This work has already resulted in one publication (Chen and Basaran 2002) and one patent (Chen and Basaran 2003).

One major future area of research is to continue and extend our work on interface rupture to situations involving two-fluid flows and the presence of electric fields. While challenging, development of scaling theories of interface rupture in single-fluid systems is much easier than that in two-fluid systems or with electric fields because the equations in the former case can be reduced to a system of one-dimensional albeit highly nonlinear slender-jet equations (see the review by Basaran 2002 for references on Newtonian fluids and Doshi et al. 2003 for pinch-off of complex fluids). In two-fluid systems and in the presence of electric fields, this reduction has hitherto proven impossible to achieve. Therefore, much computational and experimental work using high-accuracy computation and high-resolution imaging will be required to develop insights to guide the development of asymptotic theories of interface rupture in these more complicated situations. Another focus of research will be analysis of dynamics and pinch-off of two-fluid jets and drops to advance the understanding of prototypical flows that arise in microencapsulation processes. To date, such studies have relied on empiricism rather than fundamental approaches. An ongoing and yet a longer term effort is directed at development of realistic models and accurate algorithms to simulate the breakup of electrified drops and interfaces.

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STUDY OF THE HOMOGENEITY OF ADSORBENT SURFACES

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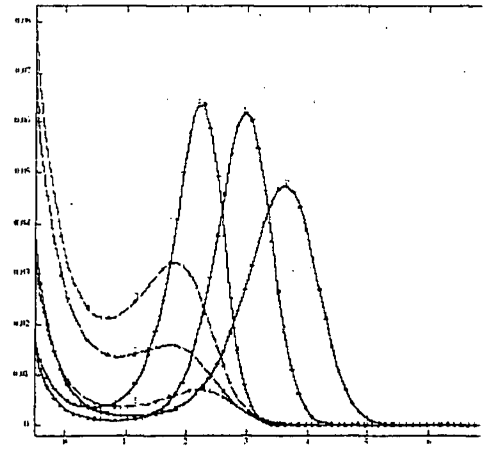
SUMMARY

The surface of all adsorbents is heterogeneous for several reasons. Impurities of the material making the bulk of an adsorbent tend to segregate at its surface (e.g., boron or iron in silica). Adsorbent surfaces are rough. The bonds between elements, particularly those involving polyvalent atoms, are strained at the fluid--solid interface. These impurities and strained bonds on the adsorbent surface cause a nonuniform distribution of the electrical field above the surface, hence of the adsorption energy of any probe close to the surface. Attempts at relating the experimental isotherms of different probes and the characteristics of their adsorption energy distribution have lead to a complex theory and an ill-posed numerical problem, with no valid tests for the lack of reference surfaces with a known adsorption energy distribution.

We developed a numerical method, the expectation–maximization method, that allows the determination of the adsorption energy distributions (AED) of probes on surfaces from their raw adsorption isotherm data, without introducing arbitrary information in the calculation process. We are applying this method to the adsorption data obtained for pairs of enantiomers on chiral stationary phases (CSP) commonly used in HPLC. Nonselective interactions always contribute to the adsorption of enantiomers on a CSP. So, the AEDs of two enantiomers consist in two modes that are relatively well resolved (enantioselective interactions are stronger than nonselective ones). The low energy mode is the same for both enantiomers (Pasteur principle). The difference between the AEDs of two enantiomers is entirely explained by the differences between the enantioselective interactions that take place between the chiral ligands of the CSP and the two enantiomers.

In the case in point, the method was applied to the adsorption data obtained with two $-blockers, alprenolol and propranolol, on a CSP made by immobilization of the protein Cel7A, a cellobiohydrolase, on silica. This protein has a long tunnel that threads and hydrolyzes cellulose molecules. This tunnel was shown to contains adsorption sites that are enantioselective for the β-blockers. We measured the adsorption isotherm data of these systems at different pH and found that these data are accurately modeled by a bilangmuir isotherm equation. One of the two Langmuir terms of this equation is identical for the two enantiomers of each β-blocker and the numerical values of its coefficients are consistent with the corresponding interactions being nonselective. The coefficients of the other Langmuir term are quite different for the two enantiomers. They correspond to a smaller saturation capacity and a stronger interaction energy. Both are different for the two enantiomers. This term accounts for the enantioselective interactions. All the coefficientsof these isotherms depend on the pH of the solution.



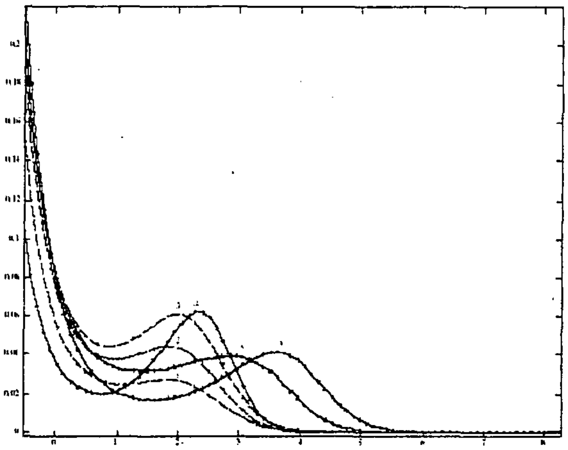


Figure 1. AED of Propranolol on Cel7A. Figure 2. AED of Alprenolol on Cel7A.

These adsorption data were used to calculate the AEDs of the two enantiomers of alprenolol and propranolol (Figures 1 and 2). The AEDs are plots of the density of sites versus the logarithm of their binding constant (that is proportional to the binding energy). The different curves correspond to the enantiomer, with the dashed lines for the (*R*)-enantiomers (# 1 to 3), and the solid lines for the (*S*)-enantiomers (# 4 to 6) that has the stronger binding energy, and to the pH of the eluent, (1) and (4) 5.01, (2) and (5) 5.51, and (3) and (6) 6.02. Clearly, the pH has a large influence on the values of the isotherm parameters, i.e., the binding constants and the saturation capacities of the two modes. The exact relationship between the adsorption energy and the binding constant is difficult to derive but the difference between the adsorption energies of two modes is simply related to the difference between the logarithms of the corresponding binding constants. The results obtained for the difference between the adsorption energies of the enantioselective modes of the two enantiomers by extrapolation of our experimental results to pH = 6.8 are in excellent agreement with the values obtained by calorimetry and reported by a different group at this pH. Unfortunately, this group did not realize the importance of the pH in the case in point. We are now in the process of measuring directly the difference between the energies of the enantioselective interactions of the two enantiomers by calorimetric measurements made with bulk solutions in the pH range of our isotherm determinations. Note that, because enantioselective interactions involve at least two strong interactions and a third, usually weaker, the energies involved in the enantioselective interactions are important. The tedious and difficult purification of the Cel7A is in progress. Other similar work is in progress for other pairs enantiomers, particularly 1-indanol.

Our work provides a new method of determination of adsorption energy distributions that can be validated by the agreement between the results of our method and independent information on the adsorption energy of the probes studied. Then, it will allow quantitative studies of the surface properties of heterogeneous adsorbents.

Separations and analysis of proteins using living polymer chains on surfaces

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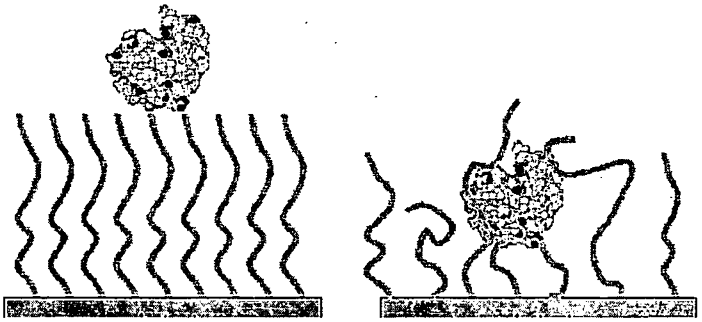
Perspective. One of the broad challenges to today's scientists is to accrue the opportunities presented by the genomics era for advancing human health. The improved separation and analysis of proteins is key to meeting this challenge. Improvements in protein separations will advance the field of proteomics for studying disease, designing devices for rapid detection of biological warfare agents, and creating new cost-effective technology for medical diagnostics. Proteins are intrinsically sticky, which has been the bane of protein separations and analysis, therefore, new surface coatings are needed to reduce unwanted protein adhesion. Our DOE-sponsored research is to investigate protein adsorption for a new class of surface coatings we invented, which is the living polymer film. These are polymer films whose thicknesses are controlled on the molecular scale. Our research focuses on the molecular-scale understanding of how these films interact with proteins. We are investigating protein interactions with these films in systems that are promising for emerging new needs in protein separation and analysis.

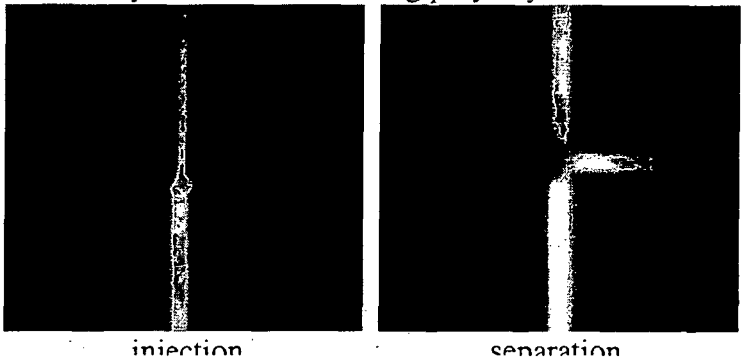
Introduction. Several years ago, with DOE support, our group developed a method of growing polymer from surfaces as if they are growing hair. A process called living polymerization is used, which means the reacting end of the growing polymer does not get destroyed by termination reactions, thus allowing the chains to grow uniformly. Since our original work, there have been hundreds of papers published in this new area because there is a great need for controlling polymerization on the molecular scale. Our interests have been in using these for protein separations. Figure 1 illustrates the concept. If one can densely grow hydrophilic, non-hydrogen bonding polymer chains from a substrate, the protein would weakly interact and also avoid entanglement, thus solving the problem of protein adsorption. We have been investigating growth of polyacrylamide, which is widely used in gel electrophoresis. This is a difficult polymerization to control by conventional methods, but it is controlled well by living polymerization. Silica capillaries and silica gel coated with living polyacrylamide performed very well in capillary electrophoresis and size-exclusion chromatography, respectively. We have two new directions to describe in this workshop: new substrates (plastics) and novel separations (hydrophobic proteins).

Figure 1. Schematic illustration of protein interaction with dense *vs.* loose polymer chains grown from a substrate.



Living polymers as coatings for plastics in microfluidic devices. Several research groups have elegantly demonstrated that microfluidic lab-on-a-chip devices perform an impressive array of chemical steps to reduce the labor in genomic analyses. Chips made of glass are the most proven. There are many groups developing chips made of plastic, including polydimethylsiloxane, polymethylmethacrylate, and polycarbonate. These materials are adhesive toward proteins. Our group is working to design the means for chemically modifying these with living polymers. The first system we have studied is polydimethylsiloxane, widely known as PDMS. This is a logical first choice because the surface can be made to look like silica by oxidization in a plasma, providing some connectivity with our expertise in chemically modifying silica. This material introduces us to the general problem of chemically modifying plastics because any organic solvent destroys the material. We developed and published a protocol for living polymerization of acrylamide on PDMS that avoids the use of organic solvents.

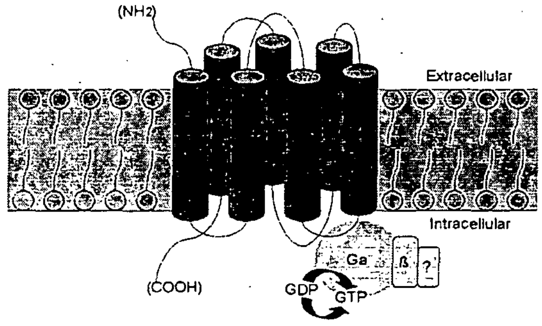
Figure 2. Fluorescence images of TRITC-labeled lysozyme in a microfluidic chip made of PDMS that is chemically modified with living polyacrylamide.



injection separation

We are now moving on to investigate the performance of polyacrylamide-coated PDMS in microchip electrophoresis of proteins. Figure 2 illustrates the injection of a protein, TRITC-labeled lysozyme, and the beginning of its travel down the separation axis. The carrier phase is aqueous buffer at pH 4. One can see that there is little irreversible adsorption because the signal remaining after the protein has been in intimate contact with the surface of the intersection is negligible after the zone has been sent into the separation channel. The problem of irreversible adsorption is thus greatly reduced by the living polyacrylamide. However, there is evidence of reversible adsorption by virtue of a wider than expected zone width. It is plausible that the density of the chains is less than we had achieved on silica. We are studying polymerization of other acrylamides that hydrogen bond less to study whether this reduces adsorption.

Figure 3.



Living polymers as supports for artificial membranes. New materials provide new opportunities to think creatively about problems. One of the big problems in proteomics is the separation and analysis of integral membrane proteins. Today's separations have been designed for water soluble proteins. Membrane proteins are lipid-soluble. Attempts to force membrane protein in the water by surfactants does not work well: 90% of the membrane protein in the human genome sequence are absent in the 2D gels used in proteomics. Membrane proteins are of paramount importance in biology. They are what the immune system recognizes, they are the gateway into cells for the action of therapeutic drugs, they control development of organisms and the response of cells to their environments. We are in the beginning stages of designing separations of membrane proteins by using the membranes themselves as the carrier media. This is illustrated in Figure 3 for a schematic G-protein coupled receptor. The living polyacrylamide would serve as a thick aqueous support medium below the membrane that would enable the membrane protein to function. A mixture of membrane proteins will be separated by an electric field and the separated proteins will serve as an addressable array to probe function. The first step has been to test the ability of the living polyacrylamide film to support a contiguous and uniform lipid bilayer, and it does. The next step, which we are doing in collaboration, will be to insert GPCRs and begin to study separation. Ultimately, the system is intended to be functional to allow more than just mass spectrometric identification of the protein. The separated proteins in the membrane allows probing of the protein functionality to studying ligand binding and the chain of events involved in signaling the interior of the cell to respond to ligand. This extends the idea of analysis to identifying biological function.

The microfluidic surfaces and membrane media described here are two venues where studying protein interactions with molecular scale polymer films can have impact. These studies are enabling for many technologies, including proteomics, drug discovery, and engineering of biosensors.

Chemical interactions between protein molecules and polymer materials: Surface chemistry affects adhesion and protein conformational changes in the bioprocessing environment

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Effective bioseparations using synthetic membranes processes depends directly on the ability to keep the membranes free of adherent molecules such as proteins and polysaccharides. These technologies are used extensively in bioprocessing and the choice of membrane chemistry is a critical element in their success or failure. Our efforts to develop and test protein adhesion resistant membranes (i.e. surfaces that exhibit minimal adhesive energy *and* minimal amounts of protein adsorption)[1-3] and to determine protein-substrate adhesion[4-7] and protein conformational stability directly address this problem.

In this presentation, we will demonstrate the influence of surface and solution chemistry on the intermolecular adhesion between proteins and different energy surfaces. We will also show how these surfaces affect the structural stability of proteins during adhesion. Using a series of analytical methods (atomic force microscopy, attenuated total reflection infrared spectroscopy, contact angle measurements, dynamic light scattering, quartz crystal microbalance and filtration experiments), we characterize the surfaces, measure the intermolecular forces, and interrogate the secondary structure of the adherent proteins. The effect of surface roughness on protein adsorption is also measured[8].

A quantitative measure of protein-substrate and protein-protein interactions is required to predict protein stability and prevent conformational changes in the bioprocessing environment. ATR/FTIR spectroscopy together with a newly-developed optimization algorithm for predicting the content of secondary structure motifs is used to correlate the secondary structure and amount of adsorbed hen egg lysozyme with the surface wettability of six different nanoporous substrates. A smooth secondary structural

conformational transition from α-helix to β-sheet, turns and unordered with decreasing wettability is observed. The role of chemical functionality of surface groups was studied using self-assembled monolayers (SAMs) with functional groups $-CH_3$, -OPh, $-CF_3$, -CN, $-OCH_3$, $-CONH_2$, $-EG_3OH$ and –OH. The secondary structural changes were measured on these substrates. Wild type and a W62G mutant of lysozyme were used as model proteins in this study. The results demonstrate that, besides mutagenesis and excursions in pH and temperature, solid substrates, characterized by their wettability, can perturb the contents of the native secondary structure of the protein and produce alternate structures rich in β-sheets.

We conclude that hydrophobic surfaces and high salt concentration result in fast protein conformational changes (α-helix to β-sheet transitions; min-hrs). Interaction with hydrophilic water-swollen surfaces at low ionic strengths has little effect on the secondary structure of these proteins.

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Abstract P4-8

METAL ION RECOGNITION THROUGH ORGANIZED MICROSTRUCTURES

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Overall research goals: The main goal of this project is to gain a fundamental understanding of the recognition of metal ions by organized molecular assemblies to obtain highly selective separations of different families of metal ions from a variety of matrices.

Specific Objectives: The specific objectives of the project for the current funding period are: 1. Investigate the mechanisms of transition and lanthanide metal ion recognition by chelating ligands in micelles and self-assembled monolayers of neutral, anionic, and cationic micelles by HPLC (high performance liquid chromatography; hydrodynamically driven separation) and CE (capillary electrophoresis; electrically driven separation) and distinguish clearly the separation mechanisms. 2. Synthesize and characterize self-assembling ligands with and without olefinic functionalities and demonstrate their metal ion recognition efficacies as self-assembled and unimolecular systems. 3. Explore nanosystems such as derivatized nanoparticles analogous to the self-assembling chelating ligand systems to obtain systems where an additional parameter namely size can influence metal ion recognition. 4. Initiate spectroscopic characterization of organized assemblies and nanosystems using the Advanced Photon Source (APS) at the Argonne National Laboratory to gain a molecular level understanding of metal ion recognition.

Significant Achievements: The following significant results have been obtained during the current grant period:

HPLC separations: 1. The mechanism of separation of transition metal ions in HPLC with a C_{18} stationary phase and the chelating ligand 8-hydroxyquinoline-5-sulfonic acid in the presence of the anionic micelles of sodium dodecyl sulfate (SDS) in the mobile phase involves the exchange of the metal ion between the ligand in the mobile phase and the SDS monolayers on C_{18}. The exchange equilibrium constant for the different metal ions was determined to be in the $10^2 - 10^4$ range. 2. The separation in the presence of cationic surfactants such as cetyltrimethyl ammonim nitrate (CTAN) results from the competition for the metal ion by the ligands in the mobile phase and the ligand on the adsorbed monolayers of surfactant on C_{18}.

Synthesis and separations with self-assembling ligands: 1. Versatile, facile, and high yield synthetic routes for self-assembling acylpyrazolones and acylisoxazolones have been investigated and several acylpyrazolones and acyliosoxzolones have been synthesized and their x-ray crystallographic structures have been determined. 2. Self-assembling acylpyrazolones exhibit unique selectivities in the separation of both transition metal and lanthanide metal ions that are not exhibited by their nonselfassembling analogs. This is illustrated in Figures 1 and 2 for 1-(4-polyoxyethylene (23) lauryl ether)phenyl-3-methyl-4-crotonoyl-5-pyrazolone (HBPMCP).

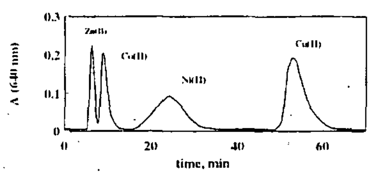

Figure 1. Separation of transition metal ions by HBPMCP.

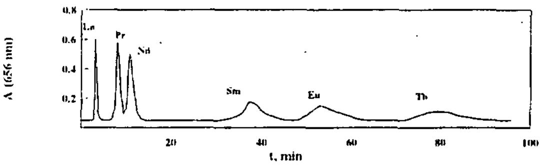

Figure 2. Separation of lanthanide metal ions by HBPMCP.

CE separation of metal ions: 1. The fundamental mechanism of separations of metal ions in capillary electrophroesis (CE) has been demonstrated for the first time. A new empirical parameter, electrophoretic equilibrium constant K_e has been defined and employed to gain a molecular level understanding of CE separations of metal ions in the presence of cationic and anionic surfactants. 2. The CE separation of metal ion in the presence of cationic surfactants results from the competition for the metal ions between the ligand in the mobile and an ordered layer of surface silanol groups on the capillary wall. The surface concentration of silanol groups was determined to be around 10^{16} groups/cm^2. 3. The CE separation in the presence of anionic surfactants result from the exchange of metal ions between the ligand in the mobile phase, the anionic micelles, and the surface silanol groups. The exchange equilibrium constant for the metal ion between the anionic micelles and the ligand have been determined these separations to be 10^6 – 10^9 depending on the metal ion.

Nanosystems: 1. The CE of gold nanoparticles derivatized with several thio carboxylic acids have been investigated to determine their solution properties to initiate our future direction on employing well-defined nanostrcutures for metal ion recognition. It has been shown that derivatized Au and Si nanoparticles have an associated electrical double layer where the net negative charge for 15 nm particles is 25 – 30, a much smaller number than that expected from geometric considerations. 2. The nanoparticles have also been shown to aggregate in surprisingly orderly manner by CE and transmission electron microscopy (TEM) in the presence of metal complexes, which could provide a mechanism for metal ion recognition.

Plans for future research on this project: This project will have two major thrusts in the future building on the current accomplishments, namely the design, synthesis, and characterization of well ordered nanosystems for metal ion recognition and a molecular level the characterization of their size dependent metal ion efficacies by a variety of imaging and spectroscopic techniques especially employing the capabilities of the Advanced Photon Source at the Argonne National Laboratory.

Publications from this project:

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Abstract P4-9

Exploring Lanthanide and Actinide Supramolecular Chemistry

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Overall research goals:

The formation of large molecular aggregates from smaller subunits, termed "supramolecular chemistry", is a field in rapid development worldwide. While future applications may include separation science and catalysis, current interest is mainly focused on the discovery of new supramolecular assemblies. These studies have greatly enriched our knowledge of metal coordination. However, to date there are very few lanthanide supramolecular assemblies reported and there is no actinide supramolecular assembly reported in the literature. Our goal is to explore and develop actinide supramolecular chemistry.

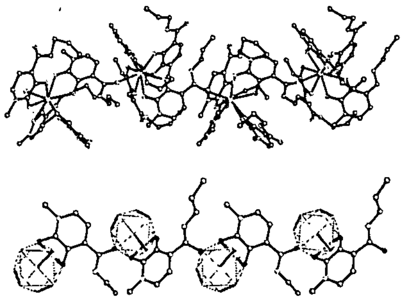
Specific objectives for 2002-2003:

Actinide coordination polymer: Discrete actinide complexes may be aggregated in the solid state or other specific conditions to form a variety of coordination polymers. Structural studies of the actinide coordination polymers will provide a better understanding of actinide coordination geometry and enable the design of new actinide supramolecular assemblies.

Quadruple stranded actinide helicates Although helicates are the most common supramolecular assemblies of metal complexes, most research in this area has focused on early transition metal complexes. The design and synthesis of quadruple bis(bidentate) stranded helicates, especially the quadruple actinide helicate, have been real challenges to chemists for more than a decade. The specific objective for 2002-2003 faced the challenge to design, synthesize, and characterize the first quadruple stranded actinide helicates.

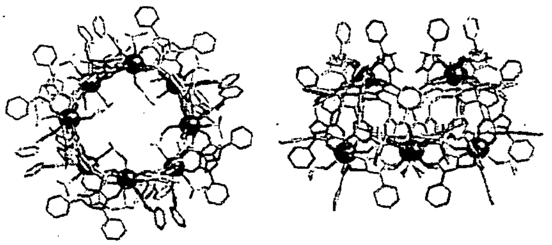
Significant achievements:

Actinide coordination polymer: In the investigation of Th(IV) complexes of bidentate 1,2-, 3,2-, and 3,4-hydroxypyridinonate ligands, it was found in the crystal of $[Th(PR\text{-}Me\text{-}3,2\text{-}HOPO)_4]\cdot H_2O$ that the chiral complex forms a linear coordination polymer composed of linked, alternating enantiomers.[1]

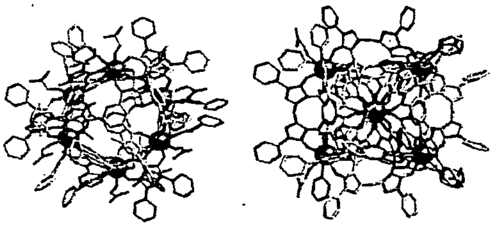


Coordination polymer composed of linked, alternating enantiomers of $[Th(PR\text{-}Me\text{-}3,2\text{-}HOPO)_4]\cdot H_2O$

La$_8$L$_8$ lanthanide ring: A lanthanum supramolecular architecture has been achieved in which nine-coordinate lanthanum centers are coordinated by three bidentate pyrazolone chelating units.[2] These centers have been combined with a rigid threefold-symmetric ligand system to drive the formation of a square antiprismatic cluster with the stoichiometry La$_8$$\mathbf{L}^{\mathbf{1}}_8$. This is the first example of a cyclic lanthanide cluster complex, a three dimensional and highly symmetric ring structure, and is an extraordinary example of symmetry-driven cluster formation.



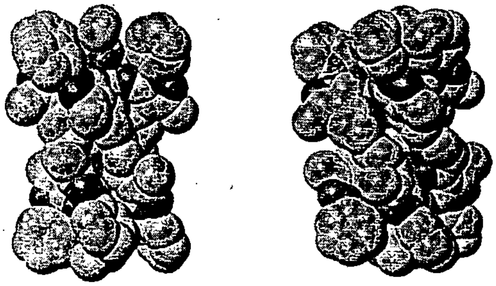
Top and side views of The Lord of Ring La$_8$L$^1_8$



Top and side views of Th$_6$L$^1_8$ Octahedral box

Th$_6$L$_8$ octahedral thorium box: We have designed, synthesized and structurally characterized the first example of a supramolecular *actinide* complex, Th$_6$$\mathbf{L}^{\mathbf{I}}_8(DMF)_6$. The cluster exhibits octahedral geometry. Shown below is the structure of the supramolecular cluster. The cluster has *eight* ligands coordinated to *six* thorium metal atoms in an octahedral arrangement. The ligand makes up the faces of the octahedron in the structure. Each ligand binds to *three* different thorium atoms and each thorium is coordinated to *four* ligands, giving the Th$_6$$\mathbf{L}^{\mathbf{I}}_8$ stoichiometry.

Quadruple stranded actinide helicates:



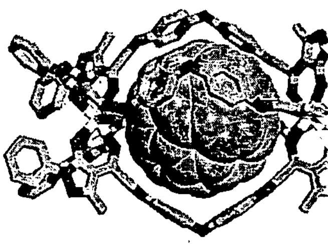
Structures of the first quadruple stranded actinide helicates

The first quadruple stranded actinide helicates Th$_2$(C3BPYZL)$_4$·2DMF and Th$_2$(C4BPYZL)$_4$·2DMF were designed, synthesized and structurally characterized. It has been stated [3] "..that the stereoselective formation of complexes from linear alkyl-bridged ligands highly depends on the preferred conformation of the spacer. Simple "addition" or "removal" of one methylene unit results in a switch from the chiral helicate to the achiral meso-helicate or vice versa." Contrary to this theory, both complexes having either an odd or even number methylene units in the alkyl bridge are chiral helicates.

Plans for future research on this project:

Design, synthesis and characterize more actinide supramolecular assembly

Host-guest chemistry of quadruple stranded actinide helicates: Preliminary modeling calculations indicate it is possible that a specially designed quadruple stranded helicate will accommodate large guest molecule such as C$_{60}$ to form a stable host-guest complex as shown right:



Computer model of the helicate-guest (C$_{60}$) complex

References of project work:

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Abstract P4-10

Principles of Chemical Recognition and Transport in Extractive Separations: Anion Recognition in Salt Extraction by Ion Receptors

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Overall research goals: This research program aims at the elucidation of the fundamental principles of ion transport by synthetic ion receptors in extractive separation systems. The core question addresses how the structure of host molecules governs their ability to recognize ionic species and effect selective, efficient separations as modulated by matrix interactions. Within this overall context, a major thrust concerns the exploration of the use of anion receptors for the enhancement of selectivity and efficiency in salt transport. Although the design of ion receptors has historically been focused on the question of cation recognition, the binding and transport of anions remains an open area with vast implications for understanding biological systems and natural processes and for developing applications such as separations and sensing.

Specific objectives for 2002-2003: A fundamental limitation in controlling anion transport is a solvation-based effect that we refer to as Hofmeister bias. It arises from the fact that the energy required to transport an anion into an organic phase is generally unfavorable and steeply biased in favor of increasing anion radius. It has been our recent objective to understand those factors that can be used to offset or overcome Hofmeister bias. These include solvation, ion-pairing, and the use of anion receptors.

Significant achievements: We have continued to systematize the extraction of salts using ion receptors based on five basic approaches: 1) no receptor; 2) cation receptor; 3) anion receptor; 4) dual-host systems (cation + anion receptor); and 5) ditopic ion-pair receptor.[1,2] In cases 1 and 2, the anion is solvated in the organic phase and subject to steep Hofmeister bias selectivity. Case 2 has been exemplified in our research by use of crown ethers and calixarenes for cesium[1-7] and even francium[3] cation extraction, in both solvent-extraction[1-6] and membrane-transport[7] systems. Hofmeister bias may be offset by solvation effects but may be nearly eliminated by strong ion-pairing.[1] Selectivity for large univalent oxoanions is maximized by exploiting the ligand-thickness effect, whereby a thick ligand effectively weakens the influence of ion-pairing.[1] If an anion receptor such as a tricarboxamide,[1,2] disulfonamide,[1,2,8] or β-fluorinated calixpyrrole[6] is used in combination with a cation receptor in a so-called dual-host system, overall cesium salt extraction is significantly enhanced.[1,2] This enhancement has been shown to be directly related to the binding constant of the anion by the anion receptor in the

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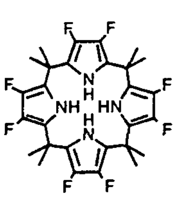
organic phase.[2] In the absence of a cation receptor, extraction of salts by anion receptors tends to be feeble at best, but use of exceptionally strong anion receptors, β-fluorinated calixpyrroles **1** and **2**, allowed us to demonstrate a rare example of Case 3 for extraction of cesium salts into nitrobenzene.[6] Even more striking and important is that the selectivity is non-Hofmeister. Smaller anions (Br^- and Cl^- for **1** and NO_3^- and F^- for **2**) were extracted as effectively as the normally much more extractable iodide.



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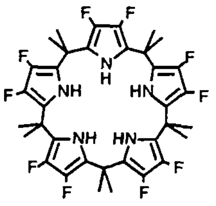

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Plans for future research on this project:

The systematics of ion-pair extraction by Cases 1–5 will be put on a more rigorous thermodynamic basis by relating overall extraction strength to individual thermochemical standard Gibbs energy terms, including those for cation partitioning, anion partitioning, cation binding in the organic phase, anion binding in the organic phase, and ion-pairing in the organic phase. This will require a speciation analysis to be conducted for Cases 3 and 4 for selected anion receptors. The systematics of anion receptors will be extended to new cases, such as synergized anion exchange. New receptors will be obtained through design and synthesis efforts, aided by productive collaborations (Hay, Sessler), and included in these studies.

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Abstract P4-11

Controlling Mass Transport Properties of Interfaces Using Ultrathin Polymer Layers

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Overall Research Goals: The goal of this project is to gain thermodynamic control over analyte adsorption and desorption at gas-solid and liquid-solid interfaces using layers of maleimide-vinyl ether alternating copolymers to create structural gradients normal to the substrate plane.

Specific Objectives for 2002-2003: We have demonstrated thermodynamic control over interfacial adsorption and desorption, characterized polymer morphology in solution and when adsorbed to interfaces, and the constructed an instrument to measure polymer adlayer dielectric (SPR) and viscoelastic (QCM) properties *in situ* and in real time for liquid-solid adsorption.

Significant Achievements: We have demonstrated the facile growth of maleimide-vinyl ether (MVE) alternating copolymers, where individual polymer layers are crosslinked using either ionic or covalent chemistry.[1-8] We have demonstrated that the adsorption and desorption characteristics of these polymer adlayers depend sensitively on the identity of the adsorbate and on the identity and number of polymer adlayers.[9] Our initial work has been with polymer bilayers and vapor phase adsorption isotherm data for methanol and *n*-hexane indicate that the form of the isotherm depends critically on the order in which the polymers are deposited on the interface.[9] The absence of hysteresis in the adsorption isotherm data demonstrates our achievement of structural control over the thermodynamics of interfacial adsorption processes using 50 Å of material.

Our goal is to achieve thermodynamic control over partitioning at thin layer interfaces by means of controlling the interfacial chemical structure (Fig. 1).[10] For a simple interface, a molecule will partition itself between the two phases according to its equilibrium constant, K, which depends on the chemical potential of the molecule in each phase. There is a step-wise change in the chemical potential at the boundary between the two phases, and K is given by the ratio of the adsorption and desorption rate constants, k_{12} and k_{21}. For interfaces composed of a structural gradient along the surface normal (Fig. 1, bottom center, right), the equilibrium constant is given by

$$K' = \frac{k'_{12}k'_{23}k'_{34}}{k'_{21}k'_{32}k'_{43}} = K_1K_2K_3$$

While K may equal K', it is unlikely that $k_{12} = k_{12}'k_{23}'k_{34}'$ and $k_{21} = k_{21}'k_{32}'k_{43}'$. By controlling the values of K_i individually through the interface layer structure, we control the kinetics of adsorption and desorption differentially.

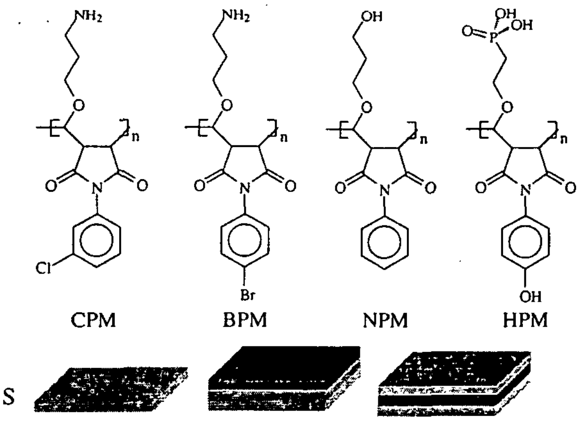

Figure 1. Top: structures of 4 MVE polymers used in this work. Bottom: schematic of substrate and bilayer-coated substrates.

The functional form of the adsorption isotherm depends on the polymer and adsorbate identities and order of polymer adlayer deposition. We use methanol and *n*-hexane as adsorbates. We obtain ΔH_{des} from fits of the data to the BET isotherm[11] and determine $K = k_a/k_d$ for each system according the Van't Hoff equation. We have acquired data for a number of interfacial bilayers, with results for S-BPM-CPM and S-CPM-BPM being typical (Fig. 2). Fits of the data to the BET equation yield $\Delta H_{des} = 31.7 \pm 4.0$ kJ/mol (K=0.5) for S-BPM-CPM and $\Delta H_{des} = 37.6 \pm 0.7$ kJ/mol (K=5.5) for S-CPM-BPM. The data for methanol adsorption on S-BPM-CPM do not exhibit hysteresis outside of the experimental uncertainty, demonstrating that we have achieved structural control over the thermodynamics of adsorbate interactions with these interfaces.[10] Interaction of methanol with a single layer of BPM produces K=4.5 and with a single layer of CPM gives K=2.9. Clearly there is a synergistic effect between the adlayers that influences primarily k_d for these systems. When these same interfaces are exposed to hexane, we recover $\Delta H_{des} = 31.8 \pm 0.4$ kJ/mol (K=5.4) for S-BPM-CPM and $\Delta H_{des} = 25.3 \pm 0.3$ kJ/mol (K=0.4) for S-CPM-BPM. Interactions between nonpolar adsorbates and the outer polymer layer play a central role in determining K, likely through k_a.

Plans for Future Research on this Project: We have been active in the design of a combined SPR –QCM system to study adsorption and desorption at the liquid-solid interface. We will also examine the relationship between solution phase polymer morphology and surface-bound polymers. We use pyrene-substituted MVE polymers and measure excimer formation as a function of pyrene substitution density. The density of pyrene side groups on the polymer determine the probability of excimer formation (Fig. 3) and the presence of excimer in excess of that predicted by a linear chain model indicates *intramolecular* interactions along the polymer chain.

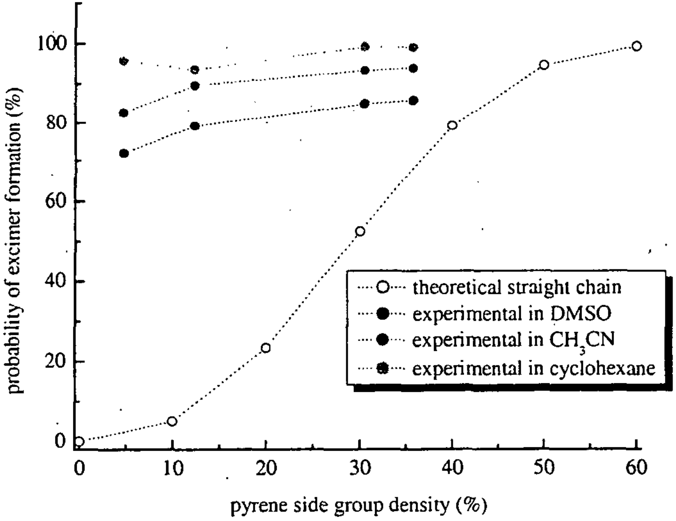

Figure 3. Comparison of theoretical prediction of pyrene side group excimer formation in solution (open circles) to experimental data (filled circles).

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Abstract P5-1

Supramolecular Assembly and the Effects of Electrostatic Interactions.

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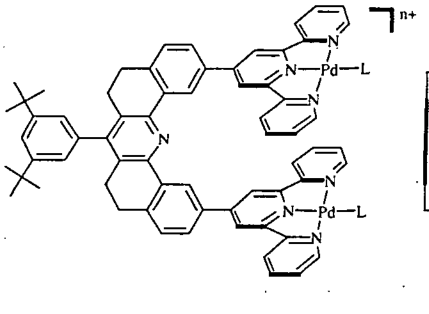
The thermodynamically controlled self-assembly of metal-based supramolecular structures relies on the kinetic lability but thermodynamic stability of metal-ligand bonds. In many cases self-assembly involves the linking of several similarly charged metal complexes to form a highly charged supramolecular structure. The electrostatic interaction within such assemblies depends on the dielectric constant of the solvent and the distances between the charges. In some cases the electrostatic interaction can be as high as ~ 50 kcal/mole, a value similar to coordination bond energies.

We have prepared the positively charged receptors of type, **1**. The effects of electrostatic interactions on the stability of the molecular assemblies were investigated for two types of systems. First, the (weak) forces of molecular recognition were used to determine if rigid ditopic molecular guests would form molecular assemblies of type, **2**, with **1** (L = Cl) and **3** and **4**.[1] The 2:1 (microscopic) association constants for **1** (L = Cl) and **4** are 1000 M^{-1} and 200 M^{-1} but the shorter guest **3** forms only a 1:1 complex with **1** (L = Cl) and the microscopic association constant value is 1,100 M^{-1}. The free energy for the first association of **1** (L = Cl) with **3** (or **4**) is -4.7 kcal/mole and the free energy for the second association constant for **4** is -3.6 kcal/mole, a difference of -1.1 kcal/mole. For 2:1 complexes formed between **3** and **1** and **4** and **1** (see **2**) the electrostatic repulsion energies (enthalpy) in DMF at 70 °C are calculated to be +3.4 kcal/mole and +2.7 kcal/mole, respectively. In the absence of electrostatic interactions the two association constants for each ditopic guest should be the same and hence the observed differences reflect receptor interactions in 2:1 complexes. The calculated electrostatic interactions are similar to those observed by experiment suggesting that electrostatic repulsion controls the association multiplicity.



L = Cl, CH_3CN

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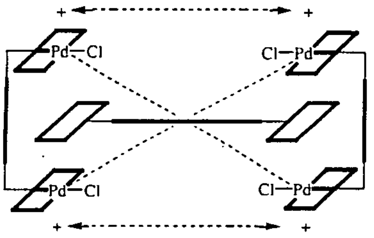

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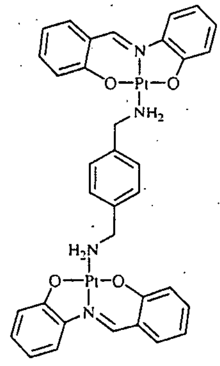

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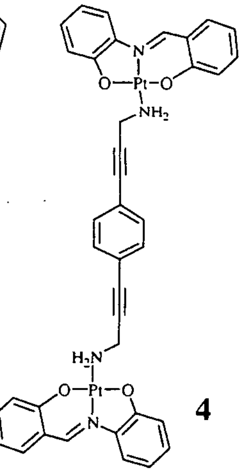

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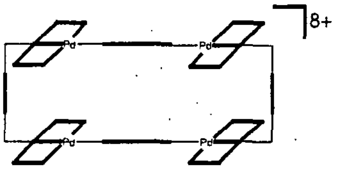
The effect of electrostatics on the formation of **5**, **6**, and **7** using coordinate bonds was investigated by self-assembly of **1** (L = CH_3CN) with **8**, **9**, and **10**, respectively.[2] The molecular rectangle and trigonal prism are readily prepared in acetone, acetonitrile or DMF solutions but the tetragonal prism is not formed in acetone or acetonitrile. Only DMF solutions support the assembly of the tetragonal prism. If electrostatic repulsion contributes to the instability of **10** then addition of a low dielectric solvent such as CH_2Cl_2 to the DMF solution of the tetragonal prism should lead to its fragmentation. This was found to be the case after more than 70% (by volume) of CH_2Cl_2 was added. Removal of the CH_2Cl_2 restored the prism in DMF.



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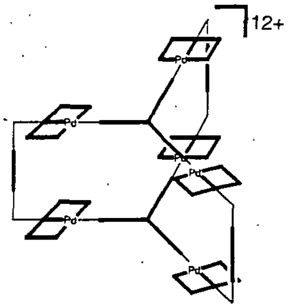

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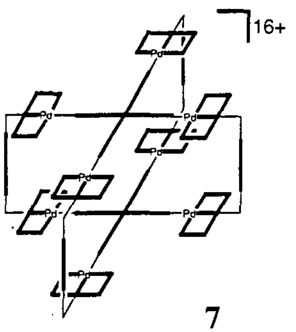

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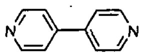

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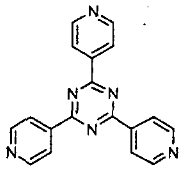

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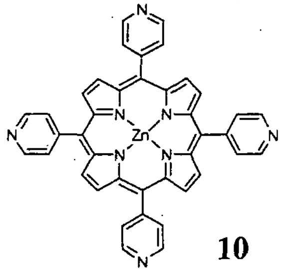

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Table 1 lists the electrostatic repulsions calculated for the supramolecular structures **5**, **6**, and **7** in various solvents. It will be noted that substantial repulsion energies obtain, some approaching coordinate bond energies. These studies have important implications in the design of metal-based supramolecular structures and in the molecular recognition displayed by the structures. Thus electrostatics are likely to play major roles in the self-assembly and stability of hosts incarcerating oppositely charged guests, in restricting the formation of catenanes with like-charged hosts and in increasing the kinetic lability of metal-based supramolecular structures.

Table 1. Electrostatic repulsion energy (kcal/mole) for the various structures.

	Repulsion Energy (kcal/mole)		
Molecular Structure	DMF($\varepsilon_{25\,°C}$ = 38.2)	CH_3CN ($\varepsilon_{25\,°C}$ = 36.2)	Acetone ($\varepsilon_{25\,°C}$ = 20.2)
Rectangle from **1** and **8**	11.4	12.0	21.5
Trigonal prism from **1** and **9**	22.9 (7.6)	24.2 (8.1)	44.3 (14.4)
Tetragonal prism from **1** and **10**	48.2 (24.1)	50.9 (25.4)	59.5 (29.7)

[a] The electrostatic repulsion released upon removal of one of the palladium receptors from the prism is shown in brackets. [b] ε is dielectric constant

References:

1. Crowley, James D., Goshe, Andrew J., Bosnich, B. (2003), Molecular Recognition. Electrostatic Effects in Supramolecular Self-assembly, *Chem. Commun.*, **(3)**, 392-393.
2. Crowley, James D., Goshe, Andrew J., Bosnich, B. (2003), Molecular Recognition. Supramolecular Self-assembly and the Influence of Electrostatic Interactions, *J. Am. Chem. Soc.*, submitted.

Other publications from this project in 2002-2003:

1. Goshe, Andrew J., Steele, Ian M., Bosnich, B. (2003), Supramolecular Recognition. Terpyridyl Palladium and Platinum Molecular Clefts and Their Association with Planar Platinum Complexes, *J. Am. Chem. Soc.*, **125(2)**, 444-451.
2. Goshe, Andrew J., Steele, Ian M., Ceccarelli, Christopher, Rheingold, Arnold L., Bosnich, B. (2002), Supramolecular Recognition: on the Kinetic Lability of Thermodynamically Stable Host-guest Association Complexes, *Proc. Nat. Acad. Sci., U.S.A.*, **99(8)**, 4823-4829.

Abstract P5-2

Organometallic Actinide Chemistry

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Prof. Alexander Voskoboynikov (Moscow State U.)
Prof. Karsten Meyer (UCSD)
Dr. Wayne W. Lukens (LBNL)

Students:
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Overall research goals:

Investigations of the chemistry of the early actinides have been conducted in nonaqueous media in order to remove the complicating factors of solvent exchange and hydrolysis, and to provide more direct comparisons of chemical reactivity (acid-base, redox), optical properties, and structural chemistry as a function of metal, oxidation state, and ligand type. These studies have proven particularly useful in the isolation of complexes with a wide array of metal-ligand bonds. Previously, studies of metal-ligand multiple bonds were limited to those involving actinyl ions (AnO_2^{n+}). As in the case of actinyl compounds, species containing other metal-ligand multiple bonds are generally found to be quite unreactive. We are currently investigating means of enhancing the reactivity of actinide-ligand multiple bonds, both in order to promote novel metal-mediated chemical transformations, and to probe the extent of covalency in chemical bonding involving 6d- and 5f-orbitals.

Specific objectives for 2002-2003:

During the past year, we have begun to investigate several methods to enhance the reactivity of metal-ligands multiple bonds, including heteroatom substitution of the multiply-bonded ligand (e.g. generation of ketimido ligands at actinide centers), and the synthesis of organoactinide complexes with new ancillary ligands (e.g. constrained geometry ligands).

Reaction of the complex $(C_5Me_5)_2UCl_2$ with two reducing equivalents (provided by KC_8), followed by reaction with excess diphenyldiazomethane generates the bis(diphenyldiazomethane) uranium complex $(C_5Me_5)_2U(=N\text{-}N=CPh_2)(\square^2\text{-}(N_2)\text{-}N=N=CPh_2)$. This is the first example of a diazoalkane actinide complex and is unlike existing transition metal diazoalkane complexes in that it possesses two diazoalkane molecules bound to a single uranium metal center: one diazoalkane is coordinated to the uranium metal center in an $\square^1$-fashion and forms a uranium imido (U=N) bond and the second diazoalkane is coordinated to the uranium in an $\square^2$-manner, possibly through the N=N □-system. Interestingly, theoretical (DFT) calculations reveal an $f^1\square^*$ electronic configuration and suggest delocalization of a 5f electron throughout the N=N=C framework of the $\square^2$-coordinated diazoalkane. Upon standing in solution, the bis(diazoalkane) complex transforms into the novel uranium bis(ketimido) complex $(C_5Me_5)_2U(\text{-}N=CPh_2)_2$. This transformation involves the unprecedented loss of N_2 from two diazoalkane fragments. The bis(ketimido) compound can also be prepared by the reaction of reduced $(C_5Me_5)_2UCl_2$ with one equivalent of benzophenone azine, $Ph_2C{=}N{-}N{=}CPh_2$. The complex is formally an f^2 system (validated by XANES) yet it does not chemically or electronically behave like known U(IV) amido complexes. Spectroscopic data support the hypothesis of donation of electronic density from the metal center onto the ketimido ligands in this system. The ketimido ligand is able to support the uranium metal center in a variety of oxidation states ranging from III to V.

Additional efforts have focused on the generation of hydrazonato complexes of uranium. Reaction of $[(C_5Me_5)_2U(CH_3)(OTf)]_2$ with diphenyldiazomethane yielded the first example of an actinide hydrazonato complex, $(C_5Me_5)_2U(\square^2\text{-(N,N)-}CH_3\text{-N-N=}CPh_2)(OTf)$. Migratory insertion of diphenyldiazomethane into both of the U-C bonds of the bis(alkyl) complexes $(C_5Me_5)_2UR_2$ (R = Me, CH_2Ph) yields the first bis(hydrazonato) complexes $(C_5Me_5)_2U(\square^2\text{-}(N_2)\text{-R-N-N=}CPh_2)_2$ (R = Me, CH_2Ph). These 22-electron complexes have no transition metal analogues. DFT calculations on the model complex $Cp_2U(\square^2\text{-}(N_2)\text{-}CH_3\text{-N-N=}CH_2)_2$, reveal that there are small but significant f-orbital based bonding interactions involving the N–N □-orbitals (HOMO-3, 6% 5f character) and the N–N □-orbitals (HOMO-9, 11% 5f character). These results demonstrate that 5f-orbital involvement can contribute to the stabilization of in-plane nitrogen 2p-lone pair combinations for which no appropriate symmetry match exists for d-transition elements. Spectroscopic and electrochemical data support the information obtained from the theoretical calculations.

Previous results on the synthesis of uranium metallocene complexes of the type $(C_5Me_5)_2U(=NPh)_2$ suggest that reactivity of the organoimido species may be enhanced both by introduction of electron-rich ancillary ligands, and by using *ansa*-metallocenes to enhance access of substrates to the imido ligands. With this in mind, we are currently investigating the generation of new actinide complexes employing constrained geometry ligands, or cyclopentadienyl-based ligands with pendant amide groups. New tetravalent actinide complexes have been generated for both uranium and thorium. Two new thorium complexes incorporating the *ansa*-cyclopentadienyl-amido ligands $C_5Me_4Si(Me)_2NHPh$ and $C_5Me_4Si(Me)_2NH^tBu$ (Cp""$Si(Me)_2NHR$; R= Ph, ^tBu) have been synthesized and characterized. The first has been crystallographically characterized as a tetramer of Cp""$Si(Me)_2NPhThCl_2$. The second has been crystallographically characterized as a dimer of $Li(Et_2O)_2$[Cp""$Si(Me)_2N^tBuThCl_3$]. In both cases the thorium centers may be viewed as having pseudo octahedral geometry, formally with two dative and two covalent chloride interactions.

Significant achievements:

Carol Burns was awarded a LANL Fellow's Publication Prize for 2002 for work conducted primarily under the OBES-funded program.

Plans for future research on this project:

We will continue our studies of low-valent organouranium complexes with diazoalkanes to understand the unusual bonding and electronic features displayed by these systems. We intend to exploit the remarkable ability of the ketimido ligand to stabilize a variety of oxidation states at uranium (III to V) to prepare novel monopentamethylcyclopentadienyl uranium(V) complexes such as $[(C_5Me_5)U(\text{-N=}CPh_2)_3][B(C_6F_5)_4]$.

We will continue our efforts to introduce new members to the family of actinide complexes containing metal-ligand multiple bonds, either by redox reactions (e.g. examining the possible cleavage of diphosphenes and the stability of the ensuing phosphinidene ligands, exploring methods for the introduction of sulfide groups using elemental sulfur or sulfur atom donors) or by ligand elimination (e.g. in the generation of uranium alkylidene complexes).

We will examine the redox characteristics of metallocene complexes employing constrained-geometry ancillary ligands to determine whether these ligands are capable of supporting high-valent uranium; subsequent reactivity studies will determine the feasibility of introducing organoimido and oxo ligands.

Building on past observation of the formation of oxouranium aggregates upon oxidation of uranium metallocenes (e.g. formation of $Cp^{\ddagger}_4U_6O_{13}(bipy)_2$, $Cp^{\ddagger} = t\text{-}Bu_3C_5H_2$), we will synthesize other aggregates incorporating alternate cyclopentadienyl ligands, and attempt to prepare analogues with bridging sulfide, selenido, and tellurido ligands.

Publications from this project in 2002-2003:

- J. L. Kiplinger, D. E. Morris, B. L. Scott, and C. J. Burns, "The First f-Element Ketimido Complex: Synthesis and Characterization of $(C_5Me_5)_2U(\text{-}N{=}CPh_2)_2$," *Organometallics*, **2002**, *21*, 3073-3075. **Featured in C&E News.**

- J. L. Kiplinger, K. D. John, D. E. Morris, B. L. Scott, and C. J. Burns, "$[(C_5Me_5)_2U(Me)(OTf)]_2$: A New Reagent for Uranium Metallocene Chemistry. Preparation of the First Actinide Hydrazonato Complexes," *Organometallics* **2002**, *21*, 4306-4308.

- J. L. Kiplinger, D. E. Morris, B. L. Scott, and C. J. Burns, "Convenient Synthesis, Structure, and Reactivity of $(C_5Me_5)U(CH_2Ph)_3$: A Simple Strategy for the Preparation of Monopentamethylcyclopentadienyl Uranium(IV) Complexes," *Organometallics* **2002**, *21*, 5978-5982.

- J. L. Kiplinger, D. E. Morris, B. L. Scott, and C. J. Burns, "Enhancing the Reactivity of Uranium(VI) Organoimido Complexes with Diazoalkanes", *Chem. Commun.* **2002**, 30-31.

- M. P. Wilkerson, C. J. Burns, and R. T. Paine "Bis[Uranyl Chloride) bis (Tetrahydrofuran)], *Inorg. Synth.*, in press.

- C. Burns, M. Eisen "Organoactinide Chemistry: Synthesis and Characterization", The Chemistry of the Actinide and Transactinide Elements", 3rd edition, J. J. Katz, L. R. Morss, N. Edelstein, and J. Fuger, eds., in press.

- C. Burns, M. Eisen "Organoactinide Chemistry: Reactivity in Catalytic Processes", The Chemistry of the Actinide and Transactinide Elements", 3rd edition, J. J. Katz, L. R. Morss, N. Edelstein, and J. Fuger, eds., in press.

- C. Burns, M. Neu, H. Boukhalfa, K. Gutowski, N. Bridges, R. Rogers "The Actinide Elements", in "Comprehensive Coordination Chemistry", 2nd edition, T. J. Meyer and J. McCleverty, eds., in press.

Abstract P5-3

Principles of Chemical Recognition and Transport in Extractive Separations: Comparing the Performance Characteristics of Calix[4]arene Azacrown-6 with Calix[4]arene Oxacrown-6

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Victor N. Pastushok, visiting scientist
Cara L. Johnston, Jennifer L. Rumppe, students
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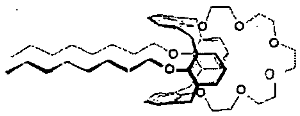
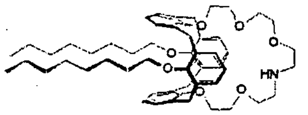
Overall research goals: The overall goal of this research program is the elucidation of ion binding and transport in extractive separations. In this context, it is important to understand how the selectivity of discrete ion pairing can be controlled by a cation receptor and an appropriate site for anion binding. Ditopic receptors can be designed by introducing a functional arm designed for anion extraction in a calixarene-crown platform proven to extract cesium selectively and efficiently. The chosen path is the replacement of one or two oxygen atoms by nitrogen atoms. Coordination of nitrogen can therefore allow for the attachment of a functionalized arm.

Specific objectives for 2002-2003: Efforts have been dedicated to determine the influence of the introduction of aza groups in the crown of the calixarene on the cesium extraction performance of the molecule.


Oxocrown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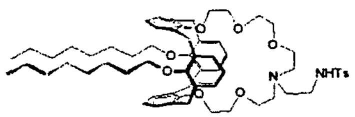
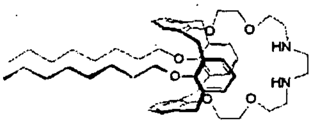
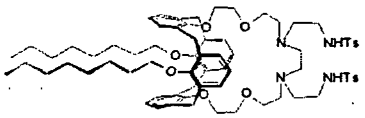

Mono-NHTs


Di-NH 3,4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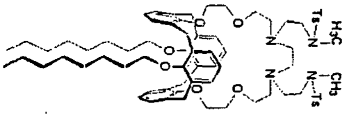
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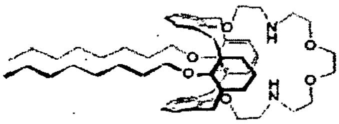
Di-NH 2,5

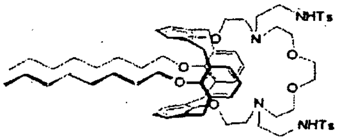
Di-NHTs 2,5

Figure 1

Significant achievements: A series of calix[4]arene azacrown-6 ethers (Figure 1) was synthesized. Cesium extraction behavior of the compounds was investigated as a function of pH, diluent, and anions present in the system and compared with that of the oxa analog. While the extraction efficiency of dioctyloxy-calix[4]arene crown-6 is not matched by any of the aza-crown derivatives, considerable progress has been made toward understanding the effect of various features of these derivatives. Figure 2 presents the results obtained for each calixarene when extracting cesium from different caustic media

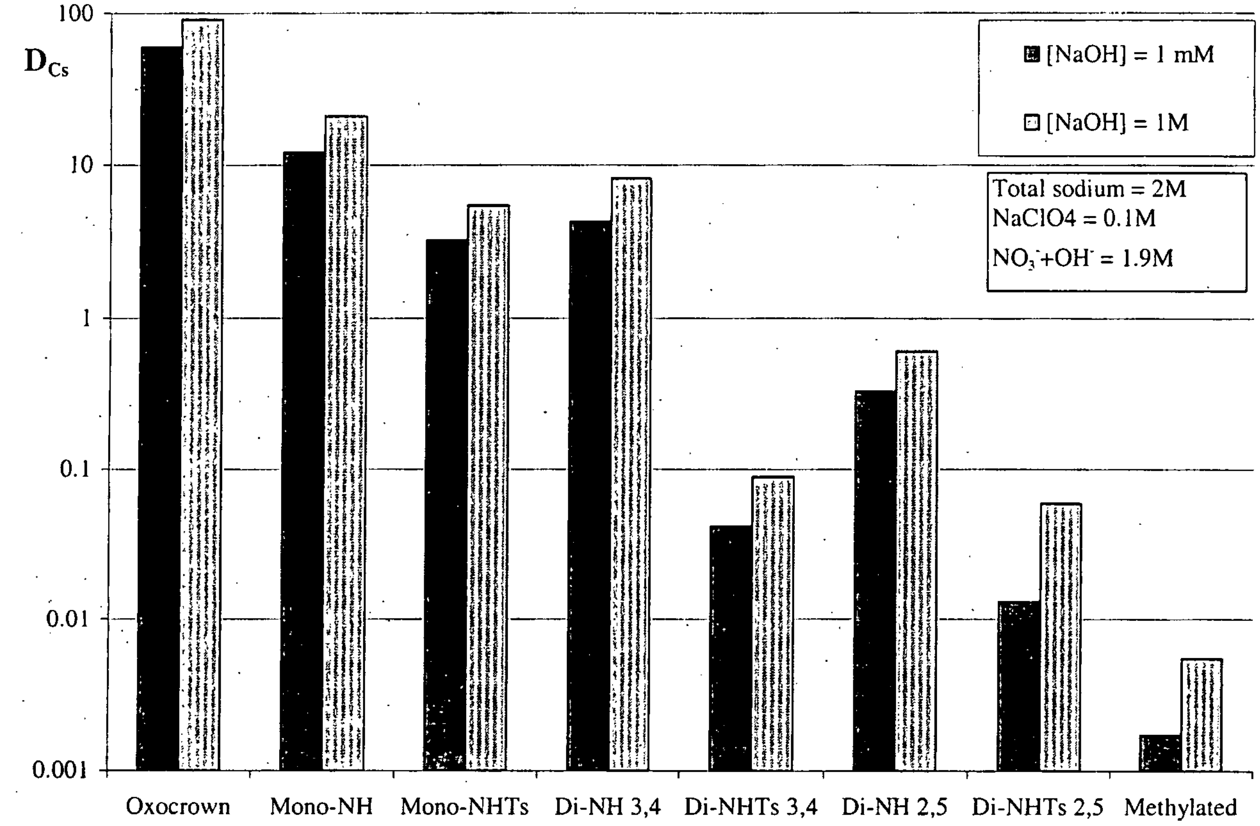

Figure 2

Replacing even one oxygen in an oxocrown with nitrogen reduces the extraction performance, and replacing a second oxygen reduces the efficiency even more.

Questions regarding the hydrogen-bonding behavior of the functional arms in the substituted compounds have been resolved. The decrease in extraction efficiency following the addition of functional arms suggests that some intramolecular hydrogen bonds are forming. The further reduced efficiency of the methylated derivative with no hydrogen-bonding capabilities, in turn, supports the idea that some of the functional arms bind anions as well. It has also been established that the free-base derivatives are protonated at pH<4 and neutral above that point.

Plans for future research on this project: A more definite answer regarding the formation of intramolecular hydrogen bonding will be sought. Studies involving infra-red experiments are being designed to gain some insight. Further experiments are also planned where the introduction of the nitrogen in the crown would no longer be viewed as a possibility to attach a functionalized arm design to help the co-extraction of the anion, but as a site that can be protonated when in contact with an acidic medium, and therefore improve the cesium stripping performance, while maintaining reasonable extraction performance in caustic media.

Other publications from this project in 2002-2003:
L. H. Delmau, C. L. Johnston, J. L. Rumppe, V. N. Pastushok, B. A. Moyer, *Comparing the Performance Characteristics of Calix[4]arene Azacrown-6 with Calix[4]arene Oxacrown-6* presentation at the 225th Spring ACS meeting, New Orleans, 2003

Abstract P5-4

PREORGANIZED AND IMMOBILIZED LIGANDS FOR METAL ION SEPARATIONS

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Postdoctoral Researchers: Iris Binyamin, Jean-Michel Camus
Graduate Student: Sahrah Parveen
Undergraduate Student: Nathan Douhart, Nick Brown
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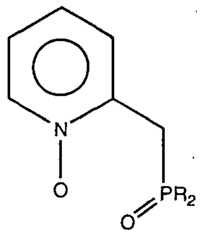
Collaborators: Mary P. Neu, (LANL); Kenneth L. Nash, (ANL);
Benjamin P. Hay, (PNNL)
Postdoctoral Collaborators: J. H. Matonic (LANL), A. E. Enriquez (LANL), C. Lavellette
(ANL), M. Borkowski (ANL), J. Uddin (PNNL)

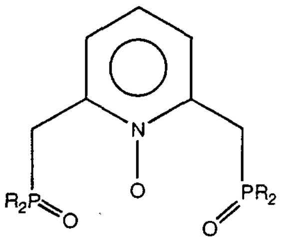
Overall research goals: The primary goal of this project is to elucidate geometric and electronic features that influence and control the binding of multifunctional chelating ligands to f-block element ions. The fundamental knowledge discovered is used to design and construct new ligand architectures that result in selective f-block ion recognition and binding under complex and harsh conditions typically encountered at DOE R&D facilities.

Specific Objectives for 2002-2003: Prior studies led to the rational design and synthesis of the new bifunctional and trifunctional ligands 2-(diphenylphosphinomethyl)pyridine N,P-dioxide **1** and 2,6-bis-(diphenylphosphinomethyl) pyridine N,P,P′-trioxide **2** (R=Ph), and characterization of coordination chemistry with lanthanide (Ln) and actinide (An) ions in which they form bidentate and tridentate chelate structures. For the 2002-2003 year, our goals have been to 1) develop syntheses for derivative ligands with solubility properties appropriate for solvent extraction; 2) study the influence of architectural changes on chelate structures; 4) explore the coordination chemistry of **1** and **2** with Pu (IV) and 3) use molecular modeling protocols to guide development of new ligand families.

Significant Achievements: During the last year, syntheses for hydrocarbon soluble derivatives of **1** and **2** have been achieved. Most notably, ligands with R= 2-ethylhexyl (2-EtHx) were prepared. In collaboration with K. Nash (ANL) the solvent extraction and thermodynamics of extraction of Am (III) and Eu (III) with **2** (R = 2 – EtHx) in dodecane were characterized. The ligand was found to have a performance similar to that displayed by CMPO ligands. The suggestion has been made that the N-oxide donor group may not bind to Am (III) under solvent extraction conditions.



1



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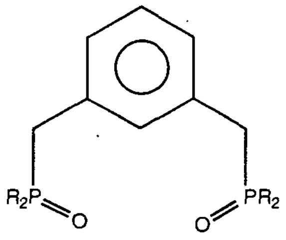
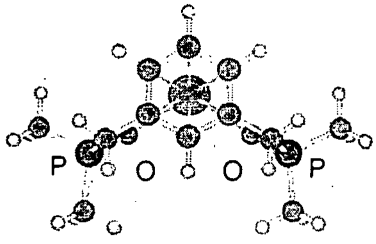
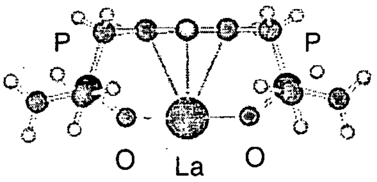


3

Abstract P5-4

The coordination chemistry of **1**, **2** and **3** (R = Ph) with Pu (IV) has been studied in collaboration with Mary Neu (LANL). In the solid state it is clear that both **1** and **2** chelate through both the phosphine oxide and the N-oxide donor groups. Interestingly, **3** without a pyridine N-oxide donor group forms a 1:1 complex with Pu (IV) in which the ligand atom positions are identical to those found in the 2:1 **2**/Pu (IV) complex, suggesting that ligand strain is minimal in these chelates. It was found that a presumed intermediate complex, Pu (**3**)(NO_3)4, in $CHCl_3$ gives the complex Pu (**3**) $(NO_3)_2Cl_2$ while in MeOH. Pu $(NO_3)_3$ (OMe) is formed. The latter appears to be the first structurally characterized Pu (IV) alkoxide complex.





Lastly, molecular modeling and DFT calculations on a La (III) complex containing **2** was undertaken in collaboration with B. Hay (PNNL). The results with **2** are completely consistent with the crystallographic studies. However, in the case of **3** the preferred structure finds the La bonded to both P = O donor groups *and* to the Π electron density in the arene ring platform as shown below.

Plans for future research on this project: The current theme will be continued during the next year. In particular, we will characterize the extraction performance of **1** – **3** and attempt to determine the involvement of the N-O donor in solution extraction complex formation. We will prepare "softened" derivatives of **1** – **3** and these ligands will be used to assess binding potential with "softer" actinide ions. Finally, we expect to continue new ligand design thrusts that may lead to further selective chelate binding conditions.

References of project work

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2. J.H. Matonic, M.P. Neu, R.T. Paine and B.L. Scott, *J. Chem. Soc. Dalton Trans.*, **2002**, 2328.
3. K.L. Nash, C. Lavallette, M. Borkowski, R.T. Paine and X. Gan, *Inorg. Chem.*, **2002**, *41*, 5849.
4. X. Gan, R.T. Paine, E.N. Duesler and H. Nöth, *J. Chem. Soc.* (Dalton), **2003**, 153.
5. X. Gan, E.N. Duesler and R.T. Paine, *Inorg. Chem.* Submitted.
6. J. Matonic, A.E. Enriquez, B.L. Scott, R.T. Paine and M. Neu, *J. Nucl. Sci. Tech.* accepted.
7. X. Gan, B.M. Rapko, J. Fox, E.N. Duesler and R.T. Paine, *Inorg. Chem.* submitted.
8. X. Gan, J. Fox, E.N. Duesler and R.T. Paine, *Inorg. Chem.* submitted.
9. X. Gan, E.N. Duesler and R.T. Paine, submitted.
10. S. Parveen, E.N. Duesler and R.T. Paine, submitted.

Abstract P5-5

The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded to Layered Arrays.

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College Station, Texas 77842-3012

Abstract

We have prepared azacrown ethers as layered and linear chain insoluble supermolecular arrays. This is accomplished by binding phosphonomethyl groups to the aza nitrogens by means of a Mannich reaction. The phosphonic acids then react with metals to form the arrays of crown ethers on $ZrPO_3$-layers or cadmium or zinc phosphonate linear arrays. A series of hexaaza and octaazacrown ethers has also been prepared and characterized. The role of these materials in separations of cations is being pursued by determining selectivities for specific cations. A related set of compounds, zirconium iminodiacetates has been found to exhibit separation factors of 1000 for separation of nuclear mother-daughter radioisotopes that are useful for nuclear medicine procedures.

Abstract P5-6

Research in Actinide Chemistry

G. R. Choppin
Department of Chemistry and Biochemistry
Florida State University

P.I.: Gregory R. Choppin

Graduate Student:
Glenn Fugate

Undergraduate Students:
Christine Leggett (Sr.)
Katherine Smiley (Sr.)

Overall Research Goals:

The goal of this program is to gain improved understanding of actinide chemistry which may lead to improved actinide-specific separations and to better understanding of actinide behavior in the environment

The relatively high specific activity of plutonium and trans-plutonium actinides limits the concentrations and, consequently, the variety of experimental techniques that can be used. Oxidation state analogs – e.g., Ln(III), Th(IV), $Np(V)O_2^+$ and $U(VI)O_2^{2+}$ - do not suffer from these limitations and are used with a wide range of experimental methods such as potentiometry, calorimetry, visible, IR and Raman spectroscopy, NMR (^1H, ^{13}C, ^{139}La), laser induced luminescence, stopped-flow kinetics, etc.

Objectives and Achievements ('02 - '03)

A. Aminodiacetic acids as separating agents (G. Fugate):

To gain a better understanding of the effects of structural constraints and of electronic polarization effects, the complexation of f-elements has been studied with iminodiacetic acid (IDA), dipicolinic acid (DPA), dipiperidine-2,6-dicarboxylic acid (PDA) and chelidamic acid (CA).

Stability constants of the complexes (β_{101}, β_{102}) of Ln(III) cations with these ligands were determined by potentiometric titrations and the thermodynamic values of the complexation, by calorimetric titrations. ^1H and ^{13}C nuclear magnetic resonance spectra, optical spectra of the ($f \rightarrow f$) hypersensitive electronic transitions of Eu(III) and Ho(III) and the fluorescence spectra of Eu(III) were studied to gain further information on the complexes. Their speciation was determined using Eu(III) fluorescence techniques.

DPA complexes with trivalent f-element cations as a tetradentate legand while CA forms tridentate compleses. Consequently, the stability constants for the Ln(III) cations are smaller than those for complexation with DPA, with a smaller variation in the stability constants across the Ln(III) series. PDA formed weak 1:1 complexes and was less studied.
A larger variation of the stability constant across the series of Ln(III) ions has been shown to result in improved separations of the individual ions. Structural rididity typically decreases the

stability constant for each LN(III) but can increase the differences in the stability constants across the series.

In summary, this work investigated the role of steric effects on piperidined-2,6-dicarboxylic acid (PDA), 2,6-dicarboxypiperidine-N-acetic acid (DPA) and chelidamic acid (CA). The stability of the complexes with these ligands are compared with that of the Ln(III) cations with iminodiacetic acid (IDA), nitrilotriacetic acid (NTA) and dipicolinic acid (DA) to better understand the effects of structural and charge modifications on the separation factors.

B: Taci and derivatives as separating agents (Daphne, Christine Leggett and Katherine Smiley):

A second ligand system under study is 1,3,5-triamino-2,4,6-trihydroxycyclohexane (taci) and several derivatives. The values of log β_{32} were measured to be 25.3 (Nd) to 33.7 (Lu). ^{1}H NMR spectra were consistent with formation of a single complex over pcH 6-10. Laser fluorescence measurements of the $^7F_0$ - $^5D_0$ transition of Eu(III) complexed by taci indicated a single complexed species. Luminescence lifetime measurements indicated 6 inner sphere water molecules for Eu(III) in the taci complex. Similar studies have been done with the 1,3,5-tridioxy2,4,6-tris(2-hydroxybenzyl)amino-cis-inosital (thci) to investigate the role of steric effects in the complexation of these cyclohexyl ligands.

These results are being analyzed in terms of structural and charge effects for designing agents for highly and efficient isolation of actinides from contaminated equipment, building materials and soils.

Publications:

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Abstract P5-7

NEW PROTON-IONIZABLE, CALIXARENE-BASED LIGANDS FOR SELECTIVE METAL ION SEPARATIONS

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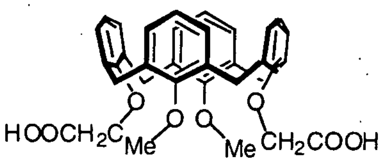
New metal ion extractants have been prepared by attaching acidic groups to the lower rim of a calix[4]arene scaffold. By matching the number of proton-ionizable groups to the valency of the metal ion to be extracted, ion exchange provides an electroneutral extraction complex thereby avoiding co-extraction of an aqueous phase anion. This is a critical factor for potential practical applications in which hydrophilic anions, such as chloride, nitrate, or sulfate would be involved.

To determine the influence of conformation on efficiency and selectivity of metal ion complexation, calix[4]arene dicarboxylic acids **1-5** were prepared. In **2-5**, replacement of the OMe groups in conformationally mobile **1** with OBu groups locks the ligands in the cone, partial cone (butyl up), partial cone (acid up) and 1,3-alternate conformations, respectively. In solvent extraction from aqueous solutions into 1,2-dichloroethane, competitive extractions of alkaline earth metal cations and single species extractions of Pb(II) were performed with ligands **1-5**. For competitive extraction of alkaline earth cations, high extraction efficiency was noted for **1-3**, with low extraction efficiency for **4** and heavy precipitate formation for **5**. For **2**, the extraction selectivity order was $Ba^{2+}>Ca^{2+},Sr^{2+}>Mg^{2+}$; whereas for **1** and **3**, the order was $Ca^{2+}>Ba^{2+}>Sr^{2+}>Mg^{2+}$. Close agreement of the extraction selectivities for **1** and **3** suggests that the preferred conformation for conformationally mobile ligand **1** in the complex is partial cone (methyl up). For single species extraction of Pb(II) by ligands **1-3** and **5**, quantitative loading was observed, with much less efficient extraction by **4**. The results obtained for alkaline earth cation and Pb(II) extractions reveal that ligand **4** in the partial cone (acid up) conformation is ineffective in divalent metal ion complexation.



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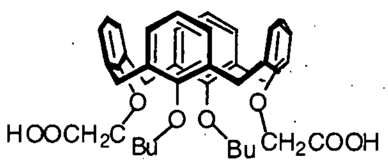

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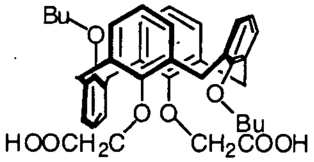

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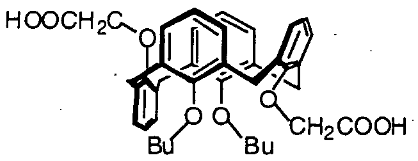

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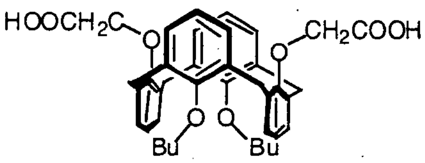
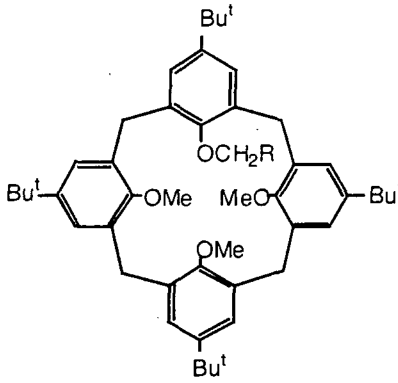


5

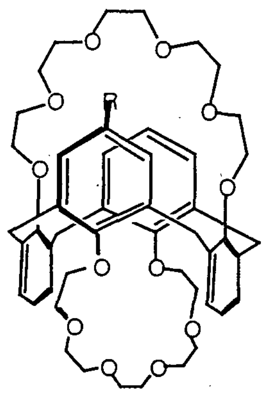
Although calix[4]arene compounds usually exhibit selectivity for complexation of Na^+ among the alkali metal cations, conformationally mobile calix[4]arene carboxylic acid **6** is highly Li^+ selective in competitive solvent extraction of alkali metal cations from aqueous solutions into chloroform (1).

Linking alternate aromatic units of a calix[4]arene with polyether units gives calix-biscrown compounds. Although the high Cs^+/Na^+ selectivities of calix[4]arene-biscrown-6 is very attractive for removal of ^{137}Cs from nuclear wastes and nuclear fuel reprocessing solutions, transport and extraction efficiency are low since both Cs^+ and NO_3^- must be transferred into the

Abstract P5-7



	R
6	CO_2H



	R
7	$C(O)NHSO_2CF_3$
8	$C(O)NHSO_2C_6H_4NO_2$-4
9	$C(O)NHSO_2Ph$
10	$CONHSO_2Me$
11	CO_2H

organic medium. In earlier work (2), we reported the synthesis and evaluation of mono-ionizable calix[4]arene-biscrown-6 **7**, for which the extraction mechanism is ion exchange instead of ion-pair extraction. Thus, for competitive solvent extraction of Na^+, K^+, and Cs^+ from aqueous solution into chloroform, ligand **7** exhibited high Cs^+ selectivity and efficiency.

Subsequently the ligand's acidity was systematically decreased in the series of related mono-ionizable calix[4]arene-biscrown-6 compounds **8-10** (3). All of the *N*-(X)sulfonyl carboxamides **7-10** were found to be more effective Cs^+ extractants than the corresponding carboxylic acid **11**. For the mono-ionizable calix[4]arene-biscrown-6 **7**, D_{Cs}/D_{Na} and D_{Cs}/D_K remained constant as the amount of competing Na^+ and K^+ in the aqueous solution was increased. Incorporation of two benzo groups into the polyether loops of **7** further increased the Cs^+ extraction selectivity (4).

Additional results from this research project have been published recently (5,6).

To provide non-ionizable crown ether ligands for use by separation scientists in the Chemistry Division at Argonne National Laboratory, a collaborative project was undertaken to develop synthetic routes for the preparation of the three less common isomers of dicyclohexano-18-crown-6 (DC18C6). Methods have now been established for the synthesis of multigram amounts of the *trans-syn-trans-*, *trans-anti-trans-*, and *cis-trans-*isomers of DC18C6 (7-9).

This research was supported by the Division of Chemical Sciences, Geosciences, and Biosciences of the Office of Basic Energy Sciences of the US Department of Energy through grant DE-FG03-94ER14416.

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Abstract P5-8

Understanding the Solid State Chemistry of Actinyl Compounds Containing Heavy Oxoanions

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Overall Research Goals: Our research program seeks to develop the solid state chemistry of actinyl compounds containing heavy oxoanions of Se(IV), Te(IV), and I(V). These compounds are of interest for several reasons. First, both actinyl cations and heavy oxoanions have a great deal of flexibility in terms of coordination numbers, geometry, and binding modes. Therefore, small changes in composition or synthetic conditions are likely to give rise to alterations in the overall extended structures that these compounds adopt. We hope to determine the systematics of these structural transformations. Second, oxoanions such as iodate, IO_3^-, have a stereochemically active lone-pair of electrons. These lone-pairs have a tendency to align in the solid state, giving rise to acentric structures that are often polar. Hence, these compounds should also show a propensity for exhibiting important physical properties, including second-harmonic generation. Finally, high oxidation state actinides have the ability to stabilize new and unusual oxoanions of heavy main group elements. We will exploit this property in the development of new main group-actinide chemistry.

Specific objectives for 2002-2003: Our focus for the duration of this grant period is to prepare and fully characterize alkali, alkaline earth, main group, and transition metal uranyl, neptunyl, and plutonyl selenites, tellurites, and iodates by hydrothermal methods. We can then evaluate any structural relationships between compounds and correlate these spectroscopic and physical property measurements.

Significant achievements: Preparing actinyl compounds containing heavy oxoanions of Se(IV), Te(IV), and I(V) offers some unique challenges because oxoanions of chalcogens and halogens are both strongly oxidizing and thermodynamically unstable with respect to the elements and/or disproportionation in many cases. This synthetic issue was solved by utilizing hydrothermal conditions, which offers a compromise between solution chemistry under ambient conditions and high-temperature solid-state chemistry. To date we have prepared more than fifty new uranyl, neptunyl, and plutonyl iodates, selenites, and tellurites. The structures of all of these compounds have been elucidated via single crystal X-ray diffraction. In addition, the thermal behavior, vibrational spectra, and electronic structure of these compounds have been evaluated using a wide variety of spectroscopic and computational techniques. These studies have yielded many important discoveries; a few of the highlights of this work are discussed below.

The potential for discovering new polar compounds is aptly illustrated by $PbUO_2(SeO_3)_2$, shown in Figure 1, which crystallizes in a polar space group. The polarity of $PbUO_2(SeO_3)_2$ is actually ascribed to the formation of PbO_5 square pyramids, that also contain a lone pair on the Pb(II) centers, and not to alignment of the SeO_3^{2-} anions. $PbUO_2(SeO_3)_2$ doubles 1064 nm laser five times better than quartz.

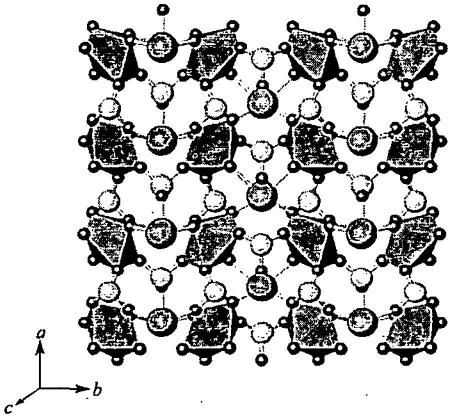

Figure 1. A view of the polar structure of $PbUO_2(SeO_3)_2$.

We have also demonstrated that high oxidation state actinides can be used to stabilize new oxanions with the discovery of tetraoxoiodate(V) anion, IO_4^{3-}. This anion was first recognized by my group in the silver uranyl iodate, $Ag_4(UO_2)_4(IO_3)_2(IO_4)_2(O)_2$. As predicted from VSEPR theory, this compound should possess a see-saw geometry induced by the presence of a stereochemically active lone-pair of electrons on the I(V) center. A more thorough understanding of this anion can be gleaned from DFT calculations that show that the observed C_{2v} geometry is the result of a second-order Jahn-Teller distortion.

Plans for future research on this project: Our current and future studies are directed toward understanding cation-cation bonding in neptunyl(V) iodates and selenites. We have now prepared five new compounds in this class, some of which contain NpO_2^+–NpO_2^+ bonds. In addition to uncovering the fundamental solid-state chemistry of these compounds, these studies also provide a unique opportunity to address magnetic coupling in Np(V) compounds where the Np(V)···Np(V) distance can be less than 3.5 Å.

Abstract P5-9

Immobilized Ligand-Modified Scaffolds: Design, Synthesis and Ionic Recognition

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Overall Research Goals: The synthesis of polymer-supported reagents with high affinities and selectivities for targeted metal ions continues to be an important problem in separations and analyses with applications to environmental remediation, wastewater treatment and sensor technology. This research centers upon ionic recognition by novel polymers with the goal of understanding the variables that determine the strength of ion-ligand interactions. Three questions are critical:
(1) Can we control where ligands are placed within a polymer matrix in relation to each other?
(2) Will the resulting ligands display enhanced inter-ligand cooperation?
(3) Will this result in polymer-supported reagents with greater ionic affinity and / or selectivity?
The questions will be answered within the context of synthesizing new reagents wherein *scaffolds* are bonded to crosslinked polymers and modified with ion-complexing ligands. Scaffolds are molecules with reactive groups allowing for the bonding of ligands in order to yield larger molecules with a well-defined three dimensional structure. The *immobilized ligand scaffolds* will maximize inter-ligand cooperation and this, based on our earlier research, should lead to significantly higher ionic affinities than would be observed in its absence.. Distribution coefficients will be quantified for a series of metal ions, including Zn(II), Cd(II) and Hg(II), that yield a range of polarizability under different pH and solution ionic strength conditions.

Simple scaffolds include diethanolamine, glycerol, and erythritol. Complex scaffolds include calix[6]arene, cyclodextrin and N-methyl-D-glucamine. The scaffolds are immobilized on organic (polystyrene) and inorganic (silica) polymers. The initial modification is via the Schotten-Baumann reaction with chlorodiethylphosphate.

Specific Objectives for 2002-2003:

* Determine an immobilization strategy for erythritol and glucamine to be immobilized onto chloromethylated polystyrene. All scaffolds are polar and the polymer is non-polar which necessitates identifying a common solvent that will swell the beads and allow reagent accessibility

* Determine an immobilization strategy for diethylchlorophosphate.

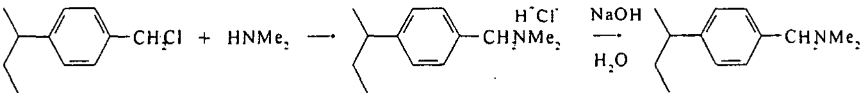
* Evaluate the ion-binding affinities of the polymers for Zn(II), Cd(II) and Hg(II).

Significant Achievements: Poly(vinylbenzyl chloride) [polyVBC], both as chloromethylated polystyrene and prepared from vinylbenzyl chloride, is widely used as the support in the immobilization of ion-selective reagents because of the ability of the -CH_2Cl groups to undergo reaction with nucleophiles.[1] In our initial reactions combining the sodium salt of erythritol with the polymer, N,N-dimethylformamide (DMF) was used as the solvent, as it is in numerous organic syntheses, because of its ability to dissolve compounds with a range of polarity differences. When synthesizing polymer-supported reagents, it is important that the structure be well-defined. When the polymer is used in ionic recognition studies, the presence of unidentified ligands will give misleading metal ion affinities. In the current research, the resulting polymer was found by titrimetric analysis to have a significant acid capacity where none was possible from the immobilized erythritol ligand. This resulted in further experiments which uncovered that DMF reacts with polyVBC to form ion-complexing ligands.[2]

PolyVBC beads were first refluxed with DMF from 2 h to 48 h. The copolymer had an initial chlorine capacity of 6.40 mmol/g (and an initial acid capacity of 0.00). Elemental analyses indicated that a reaction is occurring: after a 48 h reflux and elution of the beads with water / NaOH / water / HCl / water, the chlorine capacity decreased from 6.40 to 3.14 mmol/g and the nitrogen capacity increased from 0.00 to 3.09 mmol/g while an acid capacity determination gave a value of 2.16 mmol /g. Subsequent elution of the polymer with NaOH and water gave values for the chlorine, nitrogen and acid capacities of 0.00, 2.93 and 0.31 mmol/g, respectively. Loss of chlorine after NaOH / H_2O elution indicates that it is ionically, rather than covalently, bound. There was complete reaction at the CH_2Cl groups and total loss of chloride after an 8-hour reflux period. Reaction begins at 60°C and is complete by 140°C. The loss of covalently bound chlorine parallels the increase in nitrogen.

The presence of an acid capacity in the product of the reaction between polyVBC and DMF indicated the formation of a ligand with an exchangeable proton but it was tied to an exchangeable chloride ion. The presence of a tertiary amine group would be consistent with the nitrogen capacity and the exchangeable ions as H^+Cl^- on the polymer; this was confirmed by synthesizing a tertiary amine polymer directly (eq 1) and it behaved identically to the polyVBC / DMF product.

Formation of a -CH_2NMe_2 ligand by reaction of the polyVBC with DMF is consistent with decomposition of the DMF to carbon monoxide and dimethylamine followed by amination of the polymer. Additionally, comparison of the theoretical and experimental nitrogen capacities indicate nucleophilic attack by the carbonyl oxygen on the polyVBC (eq. 2) and this is supported by solid state ^{13}C-nmr spectra. We propose formation of -CH_2OH and -CH_3 groups along with an equal amount of dimethylamine ligands when polyVBC is heated with DMF above a threshold temperature of 60°C. The -CH_2Cl moiety in the polymer is of sufficient reactivity for attack by DMF.



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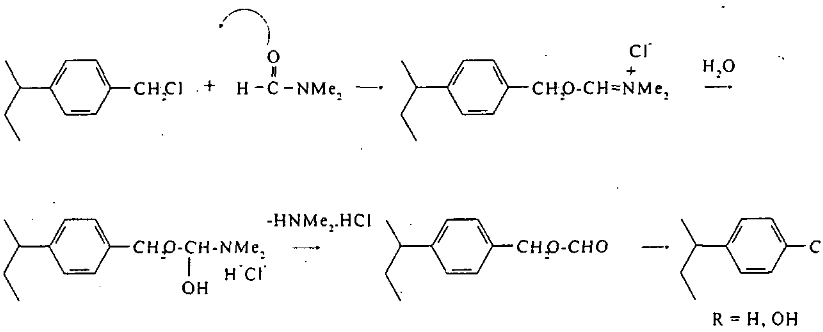

(2)

A thorough study of solvents finds that N-methylpyrrolidone has the required properties and has permitted the immobilization of erythritol and glucamine with no side reactions.

Plans for Future Research on this Project:

The remainder of the project period will focus on the modification of the scaffolds with diethylchlorophosphate and a determination of whether more than one phosphate can be immobilized per ligand. Metal ion studies will begin after the polymers have been characterized.

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Abstract P5-10

Nanostructured Hybrid Materials for Advanced Membrane Separations

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Overall research goals: This research program focuses on the development of nanostructured membranes for gas separation applications. These novel membranes are based on hybrid materials of polymers and finely dispersed nonporous, nano-scale inorganic fillers.

Specific objectives for 2002-2003:

To extend our earlier studies of the transport and separation properties of highly rigid, nonpolar polymer/fumed silica nanocomposites, which had interesting separation properties for hydrocarbon/hydrocarbon mixtures,[1] we have launched studies of the efficacy of including nanostructured, polar particles in polar rubbery polymers, such as poly(ethylene oxide), as a way to improve acid gas/light gas (e.g., CO_2/H_2, CO_2/N_2, and CO_2/CH_4) separation properties. During 2002-2003, we focused attention on highly gas-permeable, crosslinked poly(ethylene oxide acrylate) (XLPEO). This material has the advantage of having high concentrations of ethylene oxide units (82 wt. %) but, because the ethylene oxide units are attached as relatively short side chains of the polymer backbone, XLPEO does not crystallize. Additionally, crosslinking improves the mechanical properties of the resulting membrane. CO_2 permeability in XLPEO reaches 105 Barrer, and CO_2/H_2 selectivity is 7.4. As temperature is lowered from 35°C to –20°C, CO_2 permeability in XLPEO decreases to 4.6 Barrer (at 4.4 atm feed pressure), but CO_2/H_2 selectivity increases to 17, CO_2/N_2 selectivity increases to 250 and CO_2/CH_4 selectivity increases to 130. In the next phase of this work, we are planning to prepare nanocomposites based on XLPEO and nanoscale "polar carbon" particles, which have amine groups on their surfaces that could potentially augment CO_2 solubility in the polymer matrix, thereby potentially improving permeation properties.

In cooperation with Professor Toshio Masuda's group at Kyoto University, we prepared and characterized poly(1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene), PTMSDPA, a rigid polyacetylene, for use in our studies of hydrocarbon/hydrocarbon separations. This polymer is of great interest as a platform material for nanocomposite membranes. It has been reported to be highly permeable to O_2 and N_2.[2] However, its permeation properties for higher hydrocarbons, such as butane, a marker for higher hydrocarbon contaminants in natural gas, has never been tested before our studies. Interestingly, it can be readily desilylated, yielding poly(diphenylacetylene), PDPA, which is insoluble in all known solvents and cannot be prepared at significant molecular weights by any other routes. PDPA is attractive because it is expected to have outstanding chemical resistance to natural gas contaminants.

Significant achievements:

1. Gas transport properties in pure PEO have been measured, and such properties have not been reported previously in the literature, due in part to the highly crystalline nature of PEO, which reduces its permeability markedly.

2. XLPEO has been synthesized as the base material for the further study. XLPEO has better mechanical property and is more compatible with nanoscale additives than pure PEO. CO_2 permeability in XLPEO is almost one order of magnitude higher than in pure PEO. Moreover, at low temperatures, acid gas/light gas selectivity values increase strongly in XLPEO.

3. We successfully characterized PTMSDPA and PDPA as new matrix materials for nanocomposites.

Plans for future research on this project:

We will continue to focus on the fundamentals of transport in nanocomposite systems to determine the influence of nanoparticle concentration, size, surface chemistry, and overall chemical composition on separation performance.

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New Insight into the Coordination Chemistry of Plutonium and Americium: Synthesis and Structural Characterization of Pu(III) oxalates and Am(III) iodates

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Overall research goals:

Modern advances in plutonium (Pu) process and separation chemistry, prediction of weapons ageing, and long-term prediction of nuclear waste storage and disposition rely on the understanding of Pu materials on a molecular and atomistic scale. However, plutonium compounds that have been used for separation for over fifty years, such as oxalates and hydroxides,[1] remain structurally a mystery, despite their recognized importance. We have been interested in developing the solid state chemistry of transuranium elements (Np, Pu, Am, Cm), in particular, of Np, Pu, Am, and Cm compounds important for technical processes or nuclear waste performance.

Specific objectives for 2002-2003:

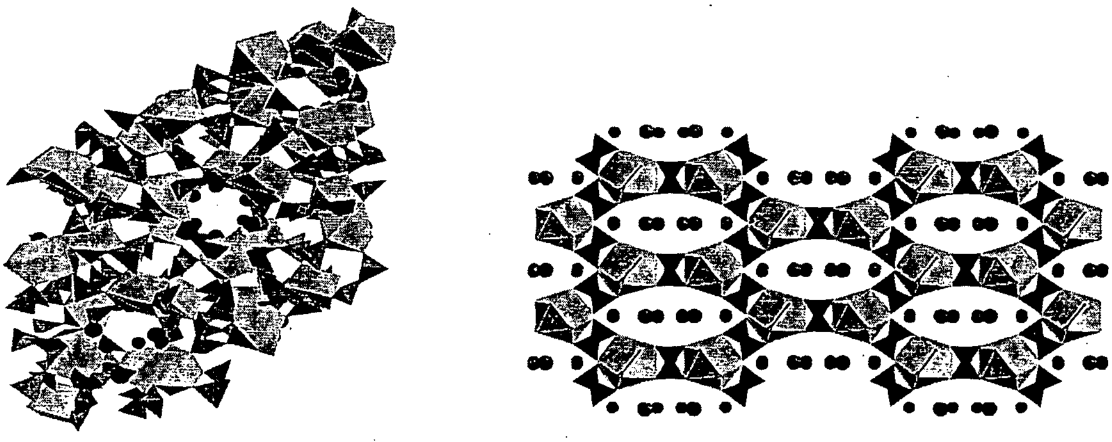
We are overcoming the obstacle of synthesizing quality single crystals of Np, Pu, Am, and Cm phases by using mild hydrothermal conditions. In the last year, we focused on the characterization of historically important Pu oxalate compounds and the synthesis of low-soluble Am(III) iodates as a potential new robust waste form.

Significant achievements:

Recently, we synthesized a series of actinyl(VI) iodates of general formula $NpO_2(IO_3)H_2O$ and $AnO_2(IO_3)_2{\bullet}H_2O$ (An = Np and Pu) showing the remarkable ability of Np(VI) to adopt both structure types displayed by its neighboring actinides.[2,3] We expanded our interest to Am(III) and synthesized three iodate phases. In addition to the common structure type in the $Ln(IO_3)_3$ series, we found a β-form of $Am(IO_3)_3$ and also obtained the first ternary americium(III) iodate, $KAm(IO_3)_4{\bullet}HIO_3$. Both compounds represent structure types that have not been observed with lanthanide elements. More important, in the three-dimensional framework of $KAm(IO_3)_4{\bullet}HIO_3$ three $[AmO_8]$ polyhedra and three $[I(5)O_3]$ groups are arranged to form irregular hexagonal channels that run along the *c*-axis with about 4.6 Å in diameter (Fig. 1 left). These channels are lined with potassium cations and filled with staggered neutral HIO_3 molecules, and may be available for ionic exchange reactions.

Oxalate has been used since over fifty years to precipitate Pu but only powder diffraction data are available for $Pu_2(C_2O_4)_3{\bullet}10H_2O$, $Pu(C_2O_4)_2{\bullet}nH_2O$ (n = 2 or 6), and $PuO_2C_2O_4{\bullet}3H_2O$.[1] We synthesized two new Pu(III) oxalates, $Pu(C_2O_4)_{1.5}(H_2O)_3$ and

$KPu(C_2O_4)_2H_2O\bullet 2H_2O$. The unique alternating bridging pattern of the oxalate groups and the $[PuO_9]$ polyhedra in $KPu(C_2O_4)_2H_2O\bullet 2H_2O$ create an open three-dimensional framework with channels along the *c*-axis (about 4.9 Å x 11.8 Å diameter (Fig. 1 right)).



$K_3Am_3(IO_3)_{12}\bullet HIO_3$ $KPu(C_2O_4)_2H_2O\bullet 2H_2O$

Figure 1: View along the *c*-axis of (left) $K_3Am_3(IO_3)_{12}\bullet HIO_3$ (the HIO_3 molecules have been removed for clarity) and (right) of $KPu(C_2O_4)_2H_2O\bullet 2H_2O$.

Plans for future research on this project:

We intend to gain insight into the rich structural chemistry of hydrous Pu(VI) oxide phases that form as alteration products from UO_2 and have been suggested as host matrix for the light actinide elements Np and Pu. Long-term stability calculations predict, however, the formation of U(VI) silicate phases, which are claimed to be unable to incorporate Pu concurring with the lack of unknown solid Pu(VI) silicate phases.

References:

1 Cleveland, J.M. *The Chemistry of Plutonium.* American Nuclear Society, LaGrange Park, IL, 1979.

2 Runde, W., Bean, A.C., Albrecht-Schmitt, T.E., Scott, B.L. (2003), Structural characterization of the first hydrothermally synthesized plutonium compound, $PuO_2(IO_3)_2\bullet H_2O$, *Chem. Comm.*, 4, 478-479.

3 Bean, A.C., Scott, B.L., Albrecht-Schmitt, T.E., Scott, B.L., Runde, W. (submitted to *Inorg. Chem.*). Structural and Spectroscopic Trends in Actinyl Iodates of Uranium Neptunium, and Plutonium.

Other publications from this project in 2002-2003:

Bean, A.C., Xu, Y.W., Danis, J.A., Albrecht-Schmitt, T.E., Scott, B.L., Runde, W. (2002), Aqueous reactions of U(VI) at high chloride concentrations: Syntheses and structures of new uranyl chloride polymers, *Inorg. Chem.*; **41**, 6775-6779.

Abstract P6-2

Principles of Chemical Recognition and Transport in Extractive Separations: Synthesis of Dibenzo-14-Crown-4 Ethers Bearing Fluoroalcohol Lariats

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Overall research goals: Previous results in our laboratories have demonstrated that dibenzo-14-crown-4 (DB14C4) ethers can form sandwich complexes with sodium ion. The formation of this bimolecular sandwich forces the accompanying anion to reside outside of the complex (Figure 1).

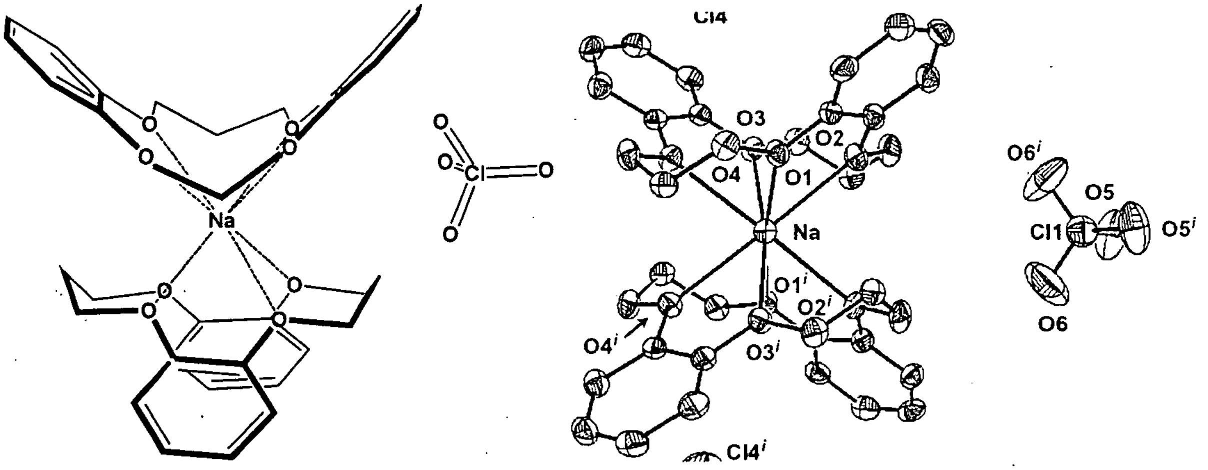


Figure 1. Sandwich complex of dibenzo-14-crown-4 with sodium perchlorate (portion of actual structure at right)

In looking at the structure, we asked ourselves the following: if a lariat with a hydrogen-bond donor group (such as hydroxyl) were appended to the center carbon of one of the propyl ether linkages, might these lariats self-assembled with sodium in the sandwich complex be able to interact in a "tweezer" fashion with an anion? Models suggested such an interaction was possible. We thus endeavored to test this hypothesis by synthesizing a series of novel DB14C4 ethers containing trifluoromethyl-substituted alcohol sidearms (Figure 2); the strong electron-withdrawing CF_3 group increases the hydrogen-bond donor ability of the alcohol. Previous studies in our group with other DB14C4 lariats revealed that for the lariat to reside equatorially (desired) instead of axially, the atom attached to the propyl bridgehead must be carbon, not oxygen.

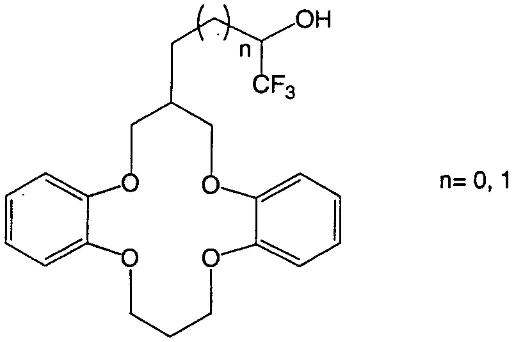
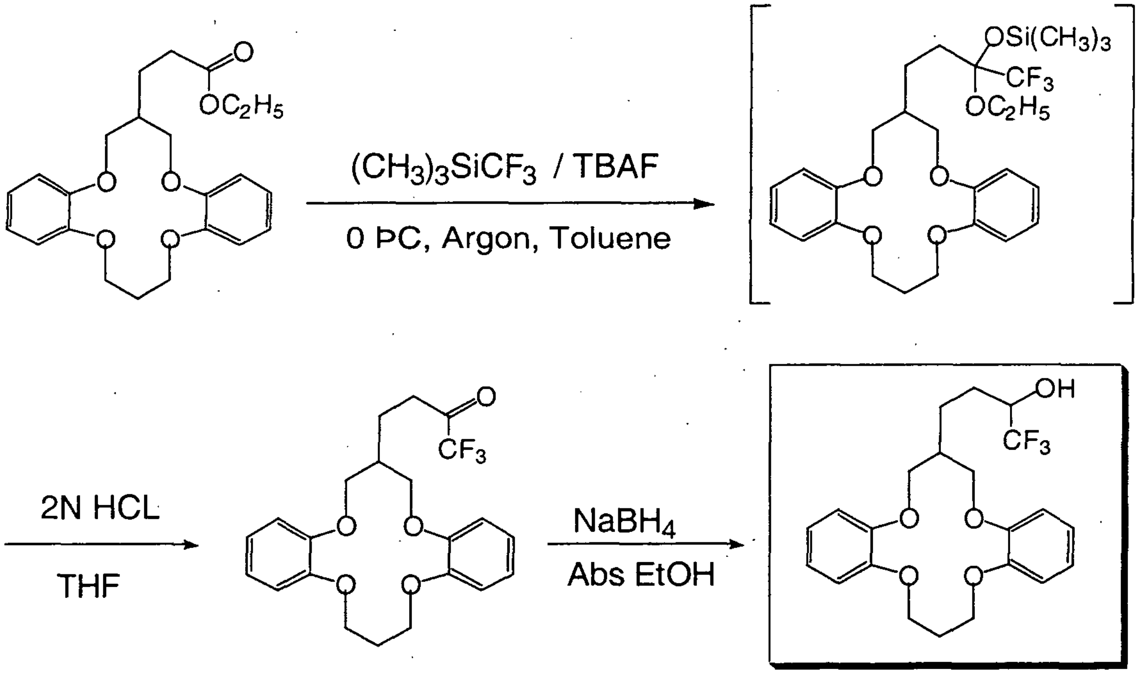


Figure 2. Two target dibenzo-14-crown-4 ethers bearing fluorinated alcohol sidearms

Specific objectives for 2002-2003: Sufficient quantities of candidate compounds will need to be prepared in very high (>99%) purity so that detailed extraction studies can be carried out.

Significant achievements: Finding a good synthetic route to this novel class of compounds was challenging, but we discovered a fairly convenient route through a readily accessible precursor. The synthesis, shown in Scheme 1 for the case where $n = 1$ (Figure 2), involves addition of a trifluoromethyl group to the ester carbonyl carbon using $TMSCF_3$ catalyzed by tetrabutylammonium fluoride (TBAF). The success of this reaction appears to be very sensitive to reaction conditions such as solvent and temperature, and we have used variable-temperature NMR experiments to probe the kinetics and mechanism of the reaction.



Scheme 1. Synthetic route to a trifluoromethyl-substituted alcohol lariat DB14C4 ether.

Plans for future research on this project: Extraction studies will be conducted with these new ionophores to test the proof-of-principle regarding whether the fluorinated alcohols upon sandwich formation can interact with the anion sufficiently to obtain enhanced ion-pair extraction. Comparison of the equilibrium extraction behavior with that of unsubstituted dibenzo-14-crown-4 together with and without 1,1,1-trifluoro-2-decanol as a separate additive will reveal whether the desired extraction behavior is being obtained. Anion selectivity will also be investigated.

Abstract P6-3

Actinide Coordination and Targeted Anion Recognition Chemistry

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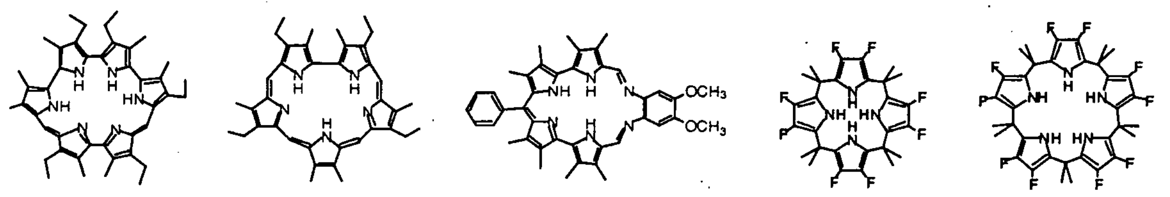
Collaborators: Drs. Web Keogh, Dave Clark, Norm Shroeder, Drew Tait, and Ms. Pam Gordon, Institute for Transactinium Science and Los Alamos National Laboratory (LANL); Dr. Bruce Moyer, Oak Ridge National Laboratory (ORNL)
Post-doctorals of collaborators: Drs. Tatiana G. Levitskaia, and Christopher Fowler, ORNL

<u>Overall research goals:</u> Develop new, expanded porphyrin-type ligands for the coordination of actinide elements and pyrrole-based receptors for the recognition, sensing, and extraction of anions of environmental importance or which relate to the DOE mission.

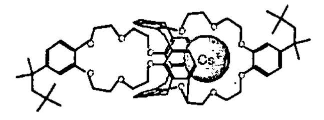
<u>Specific objectives for 2002-2003:</u> Our top goals for 2002-2003 were to:

1) Generalize the finding that a specific expanded porphyrin, isoamethyrin, could coordinate the actinide cations uranyl(VI) and neptunyl(V) by preparing other expanded porphyrins that allowed the stabilization of complexes derived from these cations, as well as plutonyl(VI).
2) Study the most promising expanded porphyrins as possible "naked eye detectable" colorimetric sensors for actinide cations.
3) Explore the interactions between sapphyrin and pertechnetate anion.
4) Test the most promising of our extant polypyrrole-based anion receptors, namely fluorinated calix[4]pyrrole and fluorinated calix[5]pyrrole, as possible anion coextractants in crowned calixarene-based cesium extraction protocols.
5) Determine whether fluorinated calixpyrroles could function as a sulfate anion extractants under high nitrate conditions that model those present in waste tanks.


isoamethyrin
sapphyrin
grandephyrin
octafluoro-calix[4]pyrrole
decafluoro-calix[4]pyrrole

<u>Significant achievements:</u>

Considerable progress was made in the context of Objective 1 as defined above. Specifically, a new class of expanded porphyrin, to which the trivial name "grandephyrin" is being assigned, was prepared.


Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
"BOBCalixC6"
(As complexed with Cs^+ ion)

In conjunction with collaborators at LANL it was found that this, as well as a range of other expanded porphyrins, was able to form complexes with uranyl, neptunyl, and plutonyl cations, as judged from spectroscopic analyses.[1] In the context of these studies, it was found that the neptunyl and plutonyl cations coordinate to expanded porphyrins more rapidly than the uranyl cation and understanding the determinants of this difference, both for a given ligand and across a series of like expanded porphyrin-type ligands is thus defined as a top future goal. It was also found that certain of the expanded porphyrins, most notably isoamethyrin, underwent a huge color change upon actinide cation coordination. Ascribed to fundamental differences in electronic structure (e.g., moving from nonaromatic to aromatic) upon complexation,[2] this finding, related to Objective 2 above, is providing the basis for possibly developing expanded porphyrins as easy-to-visualize sensors.

On the anion recognition side (Objective 3), studies involving the interactions between water soluble sapphyrin and pertechnetate anion were completed, although these have yet to be written up for publication. In conjunction with Norm Shroeder of LANL, it was found that addition of pertechnetate to sapphyrin induces substantial changes in the UV-vis spectrum as the result of both deaggregation and anion binding.

In separate anion-targeting work, it was found in conjunction with Bruce Moyer of ORNL that calix[4]- and calix[5]pyrrole could be used as adjuvants abetting the extraction of Cs+ using Moyer's crowned calixarene receptor, BOBCalixC6 (Objective 4).[3] It was also found, in work relating directly to the goal of Objective 5, that the first of these simple-to-make calixpyrroles permitted the extraction of sulfate anion from nitrate rich media at a 100:1 selectivity ratio.[4] This is the key, proof-of-concept ratio considered necessary to make such extractions a useful approach to sulfate removal in waste treatment, pre-vitrification processes.

Plans for future research on this project:

1) Explore the determinants of cation coordination selectivity, both from ligand to ligand and across the uranyl, neptunyl, and plutonyl series for a given ligand.
2) Prepare more actinide-containing liquid crystals and study their properties
3) Understand the basis for the anion selectivity and affinity displayed by polypyrrole-based receptors. What factors lead to strong binding; what factors enhance selectivity, and what factors lead to improved extraction efficiency?
4) Synthesize new actinide-coordinating expanded porphyrins
5) Design and synthesis improved sulfate anion extractants

References:

1. Sessler, J. L.; Gorden, A. E. V.; Seidel, D.; Hannah, S.; Gordon, P. J.; Scott, B. L.; Tait, C. D.; Keogh, D. W. "New Actinide Expanded Porphyrin Complexes," *Inorg. Chim. Acta.* **2002**, *341*, 54-70.
2. Sessler, J. L.; Seidel, D.; Vivian, A. E.; Lynch, V.; Scott, B. L.; Keogh, D. W. "Hexaphyrin(1.0.01.0.0): An Expanded Porphyrin Ligand for the Actinide Cations Uranyl (UO_2^{2+}) and Neptunyl (NpO_2^{+})," *Angew. Chem. Int. Ed., Engl.* **2001**, *40*, 591-594.
3. Moyer, B. A.; Fowler, C. T.; Sessler, J. L., unpublished results.
4. Levitskaia, T. G.; Marquez, M.; Sessler, J. L.; Shriver, J. A.; Vercouter, T.; Moyer, B. A. "Fluorinated Calixpyrroles: Anion-binding Extractants that Eliminate the Hofmeister Bias Selectivity," submitted to *J. Am. Chem. Soc.*

Abstract P6-4

Self-Assembled Ionophores

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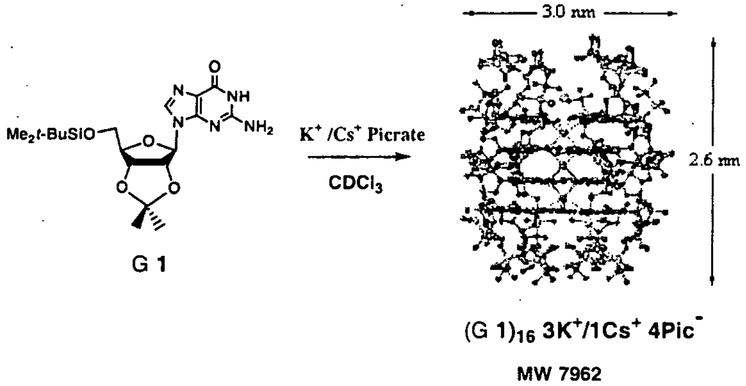
Prof. Richard Shafer, University of California, San Francisco

Overall research goals: Our goal is to build "self-assembled" ionophores that selectively bind cations, anions and ion pairs based on the guest's size, charge and shape. Instead of using covalent bonds, we have been using non-covalent interactions to synthesize such receptors. For example, lipophilic nucleosides such as guanosine **1** hydrogen bond to give assemblies that selectively bind various cations (Scheme 1). Some of these ionophores have high affinity and selectivity for ions such as Cs^+ and Pb^{+2} making them potentially valuable for separations.



Scheme 1. Lipophilic G-quadruplex $(G\ 1)_{16}\cdot 3K^+/Cs^+\cdot 4Picrate^-$ formed by self-assembly of G **1**.

Specific objectives for 2002-2003:
1) Learn how to control structure & dynamics of nucleoside self-association and cation binding.
2) Design self-assembled ionophores that selectively bind various cations and anions.
3) Construct supramolecular structures that function as synthetic ion channels

Significant achievements: In 2002, we made advances in the following areas:

Cation Ionophores. We have learned much about self-assembled ionophores formed from lipophilic nucleosides. We learned that: 1) the nucleoside's structure dictates the size, shape and ion-binding selectivity of the hydrogen bonded assembly; 2) a cation is required to template and stabilize the assemblies, 3) the ionophore-cation complexes are robust in organic solvents, 4) dynamic exchange of cations, anions and ligands is a hallmark of these complexes, and 5) these lipophilic nucleosides can selectively transport cations across hydrophobic membranes.[1,2]

Synthetic Chloride Transporters. We have identified compounds that transport Cl^- across membranes.[3,4] In effect, we have extended the self-assembly approach to also include formation of synthetic anion transporters. Using a combination of structural evidence (X-ray and NMR) and functional assays we showed that some 1,3-alt calixarene amides and some acyclic phenoxyacetamides transport Cl^- anions across synthetic phospholipid membranes.

Abstract P6-4

Biomimetics. There is much interest in understanding how DNA binds metal ions. Our assemblies are excellent models for DNA-metal interactions. Besides X-ray crystallography, there are few methods to locate cations in DNA. Lipophilic complexes from G **1** were used to validate new methods for direct observation of metal ions, namely ^{23}Na and ^{39}K solid state NMR, and extended X-ray absorption fine structure (EXAFS) using a Pb^{2+} bound G-quadruplex.[5-7]

Plans for future research on this project: Ion pair recognition is an emerging theme in supramolecular chemistry. We plan to use self-assembled ionophores to form ion pair receptors. A significant finding in our recent work is that the anion cooperates with the ligand and the cation to control structure and stability in solution. We think that self-assembly of monomeric ligands to give ditopic receptors promises to be a fundamentally new and powerful approach for selective ion pair recognition. Accordingly, we need to 1) understand the factors that control ion pair recognition and 2) design new ligands that will self-assemble to form ion pair receptors. In summary, we would like to continue to develop a self-assembly approach toward building supramolecular receptors. Our strategy is to harness the power of non-covalent and reversible interactions to select for ligands and conditions that give optimal binding of different ions, particularly environmentally important species. In addition to the potential for effecting separations, self-assembling ligands can be modified with reporter groups to provide sensors for the detection of ions. Finally, we foresee using self-assembly to build functional nanostructures, such as synthetic ion channels, mini-reaction chambers and porous membranes.

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1. "Cation-Directed Self-Assembly of Lipophilic Nucleosides: The Cation's Central Role in the Structure and Dynamics of a Hydrogen Bonded Assembly." Mangmang Cai, Xiaodong Shi, Vladimir Sidorov, Daniele Fabris, Yiu-fai Lam and Jeffery T. Davis, Symposium-In-Print on Molecular Self-Assembly, *Tetrahedron*, **2002**, 58, 661-671.

2. "G-quartets: From Supramolecular Chemistry to Molecular Biology and Back" Jeffery T. Davis, invited review *Angewandte Chemie Int. Ed.*, **2003**, submitted.

3. "Ion Channel Formation from a Calix[4]arene Amide that Binds HCl." Vladimir Sidorov, Frank W. Kotch, Galya Abdrakhmanova, Robert Mizani, James C. Fettinger and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2002**, 124, 2267-2278.

4. "Chloride Transport Across Lipid Bilayers and Transmembrane Potential Induction by an Oligophenoxyacetamide" Vladimir Sidorov, Frank W. Kotch, Yiu-Fai Lam Jennifer L. Kuebler and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, *125*, 2840-2841.

5. "The Sodium Ions Inside a G-Quadruplex Channel as Probed by Solid-State ^{23}Na NMR" Alan Wong, Scott L. Forman, James C. Fettinger, Jeffery T. Davis and Gang Wu, *J. Am. Chem. Soc.*, **2002**, *124*, 742-743.

6. "Direct Detection of the Potassium Cations bound to G-Quadruplex Structures by Solid-State K-39 NMR at 19.6 T" Gang Wu, Alan Wong, Zhehong Gan, and Jeffery T. Davis, *J. Am. Chem. Soc.*, **2003**, accepted.

7. "Pb EXAFS Studies on DNA Quadruplexes: Identification of Metal Ion Binding Site." Ivan V. Smirnov, Frank W. Kotch, Ingrid J. Pickering, Jeffery T. Davis and Richard H. Shafer, *Biochemistry*, **2002**, *41*, 12133-12139.

Abstract P6-5

Siderophore-Based Water Soluble Ligands for Actinide Decorporation

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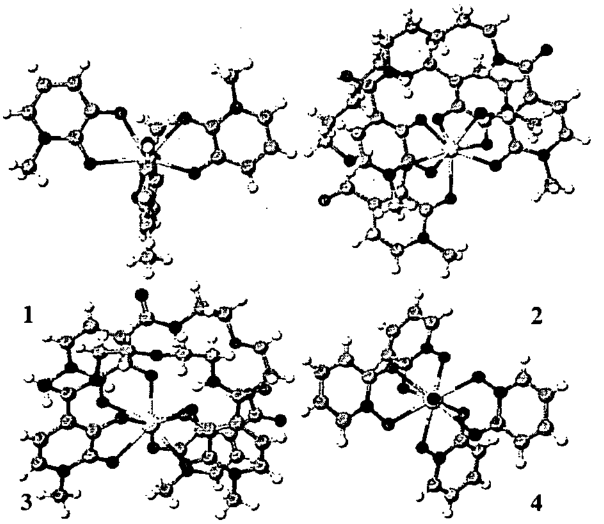
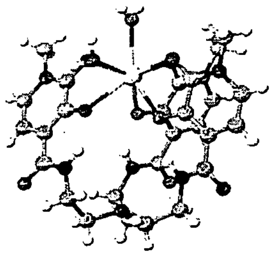
Gordon D. Jarvinen, Norman C. Schroeder, Barbara F. Smith, *Principal Investigators*
Chemical Sciences Division, Los Alamos
National Laboratory

Overall Research Goals: The aim of this project is to develop ligands for actinide decorporation based on chelating units found in siderophores, naturally occurring, iron-solubilizing compounds. Research incorporates the design, synthesis, structural and thermodynamic characterization of ligands and their metal complexes with actinides and lanthanides and the evaluation of these compounds in metal ion separations and for use as MRI (magnetic resonance imaging) contrast agents and as luminescence agents.[1,2]



Molecular structures of the Ce(IV) complexes Ce(IV)(Me-3,2-HOPO)$_4$(**1**) and Ce(IV)(5LI-(Me-3,2-HOPO))$_2$(**2**), and Ce(IV)(5LIO-(Me-3,2-HOPO))$_2$(**3**), and a similar Th(IV) complex, Th(IV)(1,2-HOPO)$_4$(**4**) designed as models for complexes of Pu(IV).

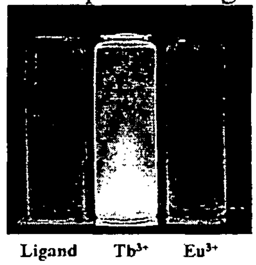
Specific Objectives of 2002-2003: Of the siderophore-based ligands evaluated for *in vivo* chelation of Pu(IV), the solution behavior of only one ligand, ETAM (ethyl 2,3-dihydroxyterephthalamide), has been characterized with Pu(IV).[3] Investigations will continue with Pu(IV) studying the solution behavior of bidentate 1,2-, 3,2-, and 3,4- HOPO (hydroxypyridonate) and SFAM (sulfonamide) ligands. We recently reported the characterization of a series of complexes with Ce(IV) including PR-Me-3,2-HOPO(**1**), 5-LI-(Me-3,2-HOPO(**2**), and 5-LIO-(Me-3,2-HOPO(**3**).[4] Similar properties to the Ce(IV) systems have been demonstrated in a Th(IV) complex (**4**).[5] Our current goal is to



Molecular structure of Gd(III)(TREN-Me-3,2-HOPO)(5), representative of potential MRI contrast agents with faster water exchange rates, high stability, and high selectivity over the physiologically important ions Ca(II), Zn(II), and Cu(II).

synthesize the corresponding Pu(IV) complexes. Concurrently, new functionalized mixed HOPO- TAM ligands for the lanthanide coordination are being designed, including modified systems for improved aqueous solubility and increased relaxivity.[6]

Significant Achievements: Since 1978, the Raymond and Durbin collaboration has produced over 120 multidentate ligands based on CAM (catecholamide), TAM, HOPO, and SFAM chelating units on a variety of molecular backbones. Over 60 of these have been evaluated for Pu(IV) chelation in mice and several evaluated in studies with other actinides, including Am(III), Th(IV), Np(V), and U(VI). The results have proven valuable in elucidating the properties underlying the effectiveness of a ligand for actinide chelation in vivo (i.e., denticity, binding group acidity, aqueous solubility).[1,2] Studies using Gd(III) complexes as models for Am(III) resulted in a Gd(III)TREN-Me-3,2-HOPO(**5**) complex; unique in that it coordinates two water molecules in the inner sphere, endowing it with superior image enhancement capabilities for use in MRI.[6] Further studies have examined complexes of the 2-hydroxyisothalamides with other lanthanides (Eu and Tb) resulting in high efficiencies converting UV to visible light and are of interest for their luminescent capabilities.[7]



Luminescence in a 2-hydroxyisophthalmide-based ligand: *left*, the ligand in solution, *center*, the Tb complex, *right*, the Eu complex.

Plans for Future Research on this Project:
Future work in this area will include the completion of the solution thermodynamics and structural characterization of bidentate TAM and/or HOPO ligands and evaluating their ability to coordinate lanthanide and actinide ions, as well as new studies to evaluate the utility of TAM-based ligands as actinide extractants in test waste samples.

References of Project Work:

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2) Gorden, A. E. V.; Xu, J.; Raymond, K. N.; Durbin, P. W. *submitted to Chem. Rev.* **2003**.
3) Gramer, C. J.; Nitsche, H.; Wilson, R. W.; Raymond, K. N. *in preparation for Inorg. Chem.*
4) Xu, J.; Radkov, E.; Ziegler, M.; Raymond, K. N. *Inorg. Chem.* **2000**, *39*, 4156-4164.
5) Xu, J.; Whisenhunt Jr., D. W.; Veeck, A. C.; Uhlir, L. C.; Raymond, K. N. *Inorg. Chem.* **2003**, *in press.*
6) Doble, D. M. J.; Botta, M.; Wang, J.; Aime, S.; Barge, A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 10758-10759, and references therein.
7) Barnes, C. M.; Petoud, S.; Cohen, S. M.; Raymond, K. N. J. Biol. *Inorg. Chem.* **2003**, *8*, 195-205.

Other Publications from this project in 2002-2003:

8) Guilmette, R. A.; Hakimi, R.; Durbin, P. W.; Xu, J.; Raymond, K. N. "Competitive Binding of Pu and Am with bone mineral and novel chelating agents," *Rad. Prot. Dosim.* **2003**, *in press.*
9) Durbin, P. W.; Kullgren, B.; Xu, J.; Raymond, K. N.; Hengé-Napoli, M. H.; Bailly, T.; Burgada, R. "Octadentate Hydroxypyridonate (HOPO) Ligands for Plutonium (IV): Pharmacokinitic and Oral Efficacy." *Rad. Prot. Dosim.* **2003**, *in press.*

Fundamentals of Solute Partitioning in Aqueous Biphasic Systems

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Overall Research Goals: The long range goal of this ongoing project continues to be the fundamental understanding of polymer-based liquid/liquid extraction. The major objectives for the current grant period include 1) Fundamental Aspects of ABS - Understanding system and solutes, 2) Chemistry in Green Solvents - Reactive extraction in ABS, 3) PEG-Gels - Application to separation processes, and 4) New Polymers and New Systems.

Specific Objectives for 2002-2003: Current objectives of the study reported here include the development of new solvatochromatic probes to extend our knowledge of the structure of and polarity of aqueous biphasic systems. Application of this work is directed toward the development of novel reaction media for chemical synthesis and reaction as Aqueous Biphasic Reactive Extraction (ABRE). Further studies of solid phase analogues of these polymeric systems are underway and the examination of novel polymers, particularly those which can be derived from renewable resources has begun.

Significant Achievements: 2002 saw the publication of a significant proportion of the ideas we have been developing over several years to elucidate the nature of ABS phase separation and the mechanisms underlying solute distribution in these systems.[1-3] Taking as the basis of our work an understanding of critical phenomena, we could rationalize that the phase separation process was marked by a difference in chemical potential between the phases which depended on the salting-out strength of the salt and the degree of polymerization of the polymer chain (Fig. 1).[1] Thus, the distribution of any given solute type could be predicted by the difference in the monomer concentration between the phases or by the reduced salt concentration as defined by $[S_R] = ([S_P] - [S_C])/[S_C]$, where $[S_R]$ is the reduced salt concentration, $[S_C]$ is the critical salt concentration, and $[S_P]$ is the salt concentration of a given biphasic system.

The distribution of large numbers of radiolabeled organic species in both PEG/salt and PEG/dextran ABS has enabled the development of a Linear Free Energy Relationship (LFER) which completely encapsulates the molecular level features of both solute and solvent that determine the equilibrium disposition of partitioned species.[3] This is illustrated in the general form of the LFER: $\log K = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_x$. Here, the log of the partition coefficient is related by multiple linear regression through a series of regression coefficients (r, s, a, b, v) and a constant (c) to the molecular properties of a solute set given by the solutes' individual descriptors including the molar refractivity (R_2), the dipolarity/polarizability (π_2^H), the hydrogen bond acidity ($\Sigma\alpha_2^H$), the hydrogen bond basicity ($\Sigma\beta_2^H$), and the volume (V_x). The sign and magnitude of the regression coefficients represent the relative properties of the two-equilibrium phases.

Our data revealed that PEG/salt ABS are dominated by differences in the hydrogen-bond donating ability of the phases, as illustrated in Fig. 2 and in the free energy of cavity formation.[2] The comparative properties of various biphasic systems are shown in Table 1. Surprisingly, the molecular hydrogen bonding features of PEG/salt and PEG/dextran ABS[4] are very similar, but the difference in the free energy of cavity formation is much reduced in the polymer system.

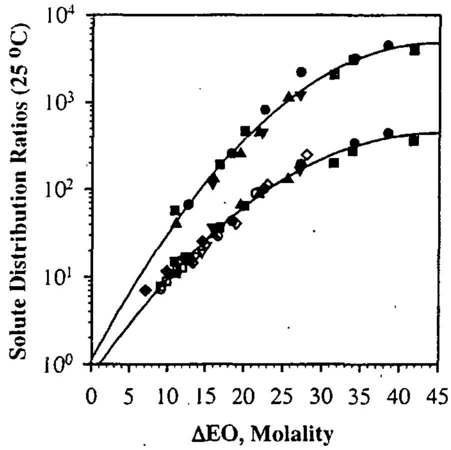

Fig. 1. Distribution ratios for benzene and 1,4-dichlorobenzene vs. ΔEO in ABS formed with 40% (w/w) PEG-2000 and various salts.

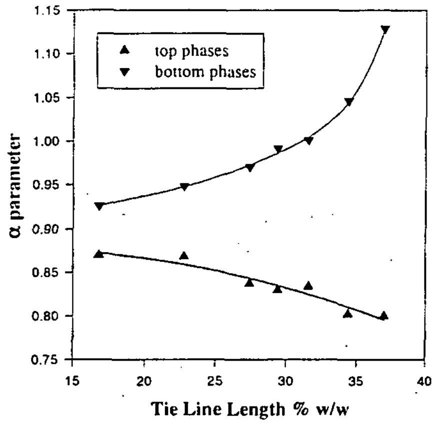

Fig. 2. α determined in the separated top and bottom phases of the PEG-2000/K_3PO_4 ABS at increasing tie line length.

Fig. 1 Key: PEG-2000 and (●) K_3PO_4; (■) K_2CO_3; (▲) $(NH_4)_2SO_4$; (▼) NaOH; (◆) Li_2SO_4; (□) $MnSO_4$; (▽) $ZnSO_4$. K_3PO_4 and (○) 40% (w/w) PEG-1000 or (◇) 40% (w/w) PEG-3400.

Table 1. Coefficients of the LSER for Two ABS

System	*c*	*r*	*s*	*a*	*b*	*v*
PEG/dextran	0.06	-0.03	0.05	0.05	-0.16	0.15
PEG/salt	-0.05	0.65	-0.21	0.21	-1.31	1.71

Plans For Future Research: Future research is directed toward the development and understanding of ABS as an alternative reaction medium for chemical processes and as the basis for biphasic reactive extraction systems. The further development of the molecular underpinning of these systems through the application of novel solvatochromatic techniques and the development of novel molecular probes will be pursued. In addition, the examination of novel materials for the promotion of aqueous phase critical phenomena, particularly those derivable from renewable resources will be actively targeted.

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3. Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. "Solvent Properties of Aqueous Biphasic Systems Composed of Polyethylene Glycol and Salt Characterized by the Free Energy of Transfer of a Methylene Group Between the Phases and by a Linear Solvation Energy Relationship," *Ind. Eng. Chem. Res.* **2002**, *41*, 2591-2601.
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Other Publications from the Project in 2002-2003: 12 and 1 Ph.D. Dissertation (Willauer, H. D.).

Abstract P6-7

Aqueous Biphasic Systems: Novel Delivery Systems and Novel Applications

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Overall Research Goals: The long range goal of this ongoing project continues to be the fundamental understanding of polymer-based liquid/liquid extraction. The major objectives for the current grant period include 1) Fundamental Aspects of ABS - Understanding system and solutes, 2) Chemistry in Green Solvents - Reactive extraction in ABS, 3) PEG-Gels - Application to separation processes, and 4) New Polymers and New Systems.

Specific Objectives for 2002-2003: We are currently using cross-linked PEG gels to advance our understanding of the behavior of free solution ABS and the nature of the co-solvency effects which lead to differential distribution of solutes in these systems. ABS are also being studied in the context of the development of Aqueous Biphasic Reactive Extraction (ABRE).

Significant Achievements: **Cross-Linked Polyethylene Glycol Hydrogels.** An extensive study has been made of the solution properties of a transparent, rubbery polyethylene glycol hydrogels constructed from the reaction of a 4-arm amino PEG (MW 10 kD) and a di-succinimidyl propyl PEG (MW 3.4 kD) as the crosslinker.[1] Using this material, we were able to gain important insights into the behavior of both the previously synthesized Aqueous Biphasic Chromatography (ABEC) resins and of the liquid ABS themselves.

It has been suggested, at the level of theory, that dehydration of the polymer and polymer collapse are important prerequisites for the phase separation of polymer/salt ABS.[1] Fig. 1 shows that the gels appear to provide a macroscopic analogue of this molecular collapse as solvent conditions change. The limiting collapse dimensions are about 0.3 to 0.4 of the original length, implying molecular collapse from an expanded helical to a loose globular or random coil state. We can reason that increase in temperature of the hydrogel should also lead to polymer collapse, and Fig. 2 shows that this is the case.[1] This collapse is associated with a decline in the polarity.[2]

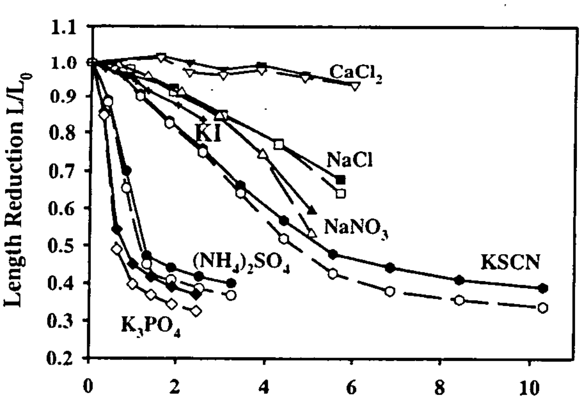

Fig. 1. Fractional length change of the PEG hydrogel in response to salt type (filled symbols hydrogel formed from 0.049 M M SPA-PEG; open symbols hydrogel formed from 0.025 M SPA-PEG).

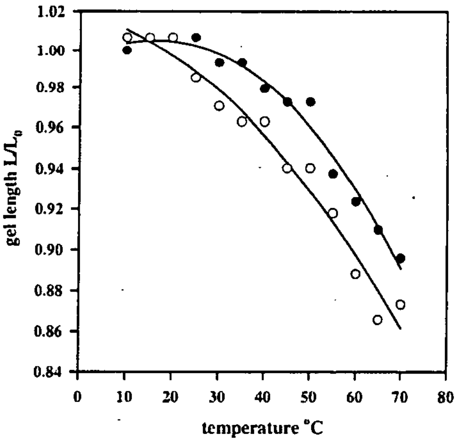

Fig. 2. Fractional length change of the PEG hydrogel in response to temperature (symbols as defined for Fig. 1).

Abstract P6-7

Aqueous Biphasic Reactive Extraction Systems. We have recently reported the synthesis of adipic acid from cyclohexene in an ABS (with H_2O_2 as oxidant and sodium tungstate as catalyst).[3] Previous oxidations of this type have relied on the use of phase transfer catalysts which are expensive to produce and difficult to recover. In this reaction, the PEG phase seems to function simultaneously as the phase transfer catalyst, the reaction solvent, and to provide the reaction driving force.[3] Sodium tungstate serves as the reaction catalyst and the biphasic system is supported by the presence of PEG-2000 and sodium bisulfate in a solvent medium which consists of a mixture of H_2O_2 and water. Table 1 shows experimental conditions which lead to significant product formation along with conditions which lead to low or practically absent amounts of adipic acid being formed. Presumably, under these conditions, rather in the manner of a phase transfer catalyst, enhanced solubility of cyclohexene in the PEG phase leads to increasing possibility of contact with oxidant (H_2O_2) and catalyst (Na_2WO_4).

The product is recovered as a precipitate in the lower phase of the ABS. Fig. 3 shows the yield of adipic acid obtained under constant conditions and constant amounts of reactants and phase forming components, but using various molecular weight fractions of PEG. Apparently, the yield increases with increasing molecular size. The effect is most marked at low molecular weight and appears to plateau at the highest polymer molecular weight.

Table 1. Adipic Acid Synthesis Reaction Conditions[a] and Product Yield.

Batch	*Reactants*		*Product Yield*
#	*PEG-2000*	*$NaHSO_4$*	*(Purity) (%[c])*
1	12.5 g	0 g[b]	Trace
2	12.5 g	3.85 g	18.1 (98)
3	12.5 g	10 g	40.1 (95)
4	5.0 g	10 g	50.0 (97)
5	2.5 g	10 g	57.2 (98)

[a] All experiments 5 g cyclohexene, 30 g 50% H_2O_2, 0.186 g Na_2WO_4.

[b] Adjusted to pH = 1.6 with 0.1 M H_2SO_4.

[c] Purity analysis is from TGA.

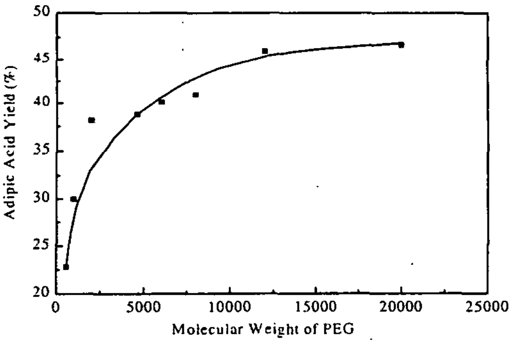

Fig. 3. Influence of PEG molecular weight on the reaction yield of adipic acid.

Plans For Future Research: Investigations of the behavior of the PEG hydrogels in a number of different solvent systems are being conducted. The mechanisms underlying the ABRE of adipic acid is being pursued and further novel chemical reactions based on ABS are being investigated.

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Other Publications from the Project in 2002-2003: 12 and 1 Ph.D. Dissertation (Willauer, H. D.).

Abstract P6-8

ACTINIDE CHEMISTRY UNDER ALKALINE CONDITIONS

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Post-doctorals: Erik Brady Garth R. Giesbrecht	Students: Anne E.V. Gorden Patricia J. Melfi		

Overall research goals:

The chemistry of the actinide ions under highly alkaline conditions has seen a resurgence over the past five years. The increased interest has been driven by multiple factors both fundamental and applied, e.g. novel chemistry in highly alkaline condition and understanding the behavior in the aging waste tanks within the DOE complex. It has been well established that highly alkaline aqueous solutions stabilize the higher oxidation states (VI/VII) for the transuranic elements, some realizing a 2 V shift in the oxidation potential. The stability of these oxidation states is dependent on the element and the total base concentration. It has also been found that the transuranic species are much more soluble than U, which forms insoluble uranates in the presence of any alkali metal hydroxide. As part of our program on the study of actinide chemistry in alkaline conditions, we have utilized a multi-disciplinary investigation to determine the speciation and reactivity of the hexa- and heptavalent ions of U, Np and Pu in tetramethylammonium hydroxide, (TMA)OH, LiOH and NaOH.

Specific objectives for 2002-2003:

1. Design and Applications of a Spectroelectrochemical Cell for the Study of Actinides in Unusual Oxidation States. A breakthrough was made in design for the spectroelectrochemical cell (SECC) for use at SSRL to generate unusual oxidation states of the light actinides. Now on the fourth generation design for the cell, positive results from the bulk electrolysis at Beamline 11-2 were finally accomplished. In the future this cell can be used to generate actinide complexes in unusual oxidation states, e.g. those that would not survive the shipping time and conditions required to move samples for spectroscopic studies. As described in greater detail below, the proof of concept for the cell was tested using Np(VI) in 3.3 M LiOH, where the tetra-oxo EXAFS and XANES signals from Np(VII) could be reversibly obtained *in situ* in the electrochemical cell. Studies have now been completed for Pu(VI) and Pu(VII) in 18 M NaOH. In addition, room temperature ionic liquids were used as electro-inactive solvents to start to produce new actinide species.

2. Uranyl Sorption under Highly Alkaline Conditions. We have completed a ground-breaking investigation into the sorption and surface-complexation of actinides on aluminous solid phases (gibbsite and alumina) under highly alkaline solution conditions (0.1 to 2.5 M OH^-). These first-ever investigations have direct implications with respect to partitioning of actinides in alkaline high-level tank wastes. Significant uptake of UO_2^{2+} species from alkaline solutions was found for both solid phases. Surface complexation was determined from luminescence spectroscopy. The principal surface complex on both solids over the entire range of [OH-] is spectroscopically similar to the $[UO_2(OH)_5]^{3-}$ species. A second, spectroscopically distinct surface complex is found on the gibbsite phase with characteristics suggestive of a molecular aggregate. Powder X-ray diffraction studies confirm that the aluminous substrates retain their integrity following contact with the alkaline solutions. In collaboration with John Rakovan (Miami Univ.) and Richard Reeder (SUNY-Stony Brook), we investigated the unusual structure of U(VI) incorporated into apatite using X-ray absorption and time-resolved fluorescence spectroscopies. The crystal lattice of apatite was found to impose an octahedral arrangement of oxo ligands around the uranium. Such a structure is not found in aqueous solution, where only the dioxo moiety is found. Such a stable octahedral structure allows the study of uranium under a highly usual coordination structure and may also bear on the development of apatite-hosted nuclear waste form.

Significant achievements:

The Spectroelectrochemical Analysis Of Heptavalent Plutonium. The heptavalent oxidation state of actinide ions has been known for nearly three decades. The majority of heptavalent chemistry has been developed for neptunium, as it displays the greatest stability for the heptavalent state among actinide elements. Based on previous work by the Russians, Argonne and ourselves, Np(VII) has been shown to exist as the unusual tetra-oxo $NpO_4(OH)_2^{3-}$ ion in alkaline solution. In order to study whether or not Pu(VII) has this same coordination geometry, we have employed a combination of cyclic voltammetry, UV-VIS-NIR, XAFS and polarized red-Raman spectroscopy to examine the characteristics of the coordination chemistry of Pu(VII) in alkaline solution. Concentrated solutions of Pu(VII) were generated in 8 – 18 M NaOH solutions by bubbling with ozone overnight. The originally brown (OH^-) or green (CO_3^{2-}) hexavalent complexes become a very dark purple. In 9 M NaOH the half-life for Pu(VII) is approximately 1 day, allowing enough time for analysis by all of the spectroscopic probes, including our new XAFS SECC capability described above. Pu(VI) solutions in 8 and 18 M NaOH were oxidized to produce Pu(VII). The experiment tracked the oxidation by observation of the absorption edge position and shape. With a significant portion of the solution oxidized the edge was observed to shift more than 1.5 eV, as expected based on the differences between the edge positions for Pu(III – VI). The EXAFS of the oxidized solution also showed significant differences that appeared to indicate an equilibrium between $PuO_4(OH)_2^{3-}$ and $PuO_2(OH)_4^-$. The oxidized solution was also electrochemically reduced to produce Pu(VI) again. The EXAFS and edge position of the resulting solution were identical to the solution prior to electrolysis, indicating the process is reversible. The proof of concept for the cell was also tested using the previously known Np(VI) to Np(VII) transition in 3.3 M LiOH. Based on these positive results the behavior of Np and Pu in room temperature ionic liquids was also studied. Compounds of the form $(PPh_4)_2AnO_2Cl_4$ (An = Np, Pu) were dissolved in a room temperature ionic liquid and solutions were analyzed by EXAFS. The analysis of the data revealed that the compounds reduced during shipment to their thermodynamically favored states, i.e. Np(V) and Pu(IV). After the initial EXAFS experiments were completed both solutions were electrolyzed in the X-ray beam to produce the hexavalent ions AnO_2^{2+}. From the analysis of the EXAFS data, the dioxo cations were also bound to Cl^- anions as well as to the anion from the ionic liquid.

Plans for future research on this project:

Electrochemical studies will continue to be performed at SSRL that will provide the ability to study the coordination geometry of the transuranics in unusual and unstable oxidation states. For highly alkaline conditions we will focus on An(V) and An(VII). The solid-state structures, EXAFS, NMR, Luminescence, Raman spectroscopic properties, and redox potentials of An^{4+}, AnO_2^{+}, AnO_2^{2+} and AnO_2^{3+}/AnO_4^{-} ions (Np, Pu) in highly alkaline solution will continue to be investigated. The electrochemical work and speciation determination will continue to be expanded into other solvent systems, e.g. organic and room temperature ionic liquids, in order to stabilize novel coordination complexes of the light actinide elements.

Sorption and surface complexation studies of actinides under highly alkaline tank waste-like conditions will continue. More detailed sorption isotherm data will be collected for the uranyl/gibbsite (alumina) systems to provide a thermodynamic basis for sorption. Additional studies will focus on spectroscopic determinations of surface complexes of UO_2^{2+} and $NpO_2^{+/2+}$ on aluminous solids. In later years, investigations including incorporation/coprecipitation reactions from aluminum and carbonate containing solutions will be undertaken. We will characterize plutonyl hydroxide phases and measure their operational solubility. With the solution and solid-state species characterized, we will progress into sorption experiments.

<u>Publications from this project in 2002-2003:</u>

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Abstract only Abstract P6-9

Studies of Solvation Processes in Supercritical Fluids and Room Temperature Ionic Liquids

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Overall research goals: The proposed research seeks to develop a molecular-level understanding of processes occurring within environmentally friendly solvent systems that are important to the DOE mission. The proposed research is divided into three (3) sub-projects.

Oligomer/polymer tail and junction point accessibility, dynamics, and mobility in pure and cosolvent-modified supercritical CO_2.

Solute-fluid interactions at interfaces in contact with pure and cosolvent-modified supercritical CO_2.

Solvent properties of room temperature ionic liquids (RTILs) as a function of dissolved cosolvents and pure CO_2.

Specific objectives for 2002-2003: In liquids, polymer conformation, dynamics, and reactivity depend on whether the polymer is dissolved in a "good", "theta" - "2", or "poor" solvent. Thus, one can control polymer behavior, growth, and/or reactivity by switching from one solvent to another. Although solvent switching does offer a strategy to control a polymer system, many liquids (e.g., CH_2Cl_2) are not particularly environmentally responsible.

Recent work from our laboratories has investigated the tail-tail dynamics of linear poly(dimethylsiloxane) (PDMS) and a PDMS-based junction point when they are dissolved in toluene (good), ethyl acetate (theta) and methanol (poor), CO_2-expanded toluene, ethyl acetate and methanol, and in pure $scCO_2$. The results of these experiments show the tremendous range of dynamics and conformations possible in these systems and how one can use CO_2 to switch the dynamics.

Supercritical fluid chromatography (SFC), supercritical fluid extractions (SFE), and supercritical fluid-based cleaning (SFBC) are extremely powerful tools. In each technique an interface of sorts plays a key role in the separation outcome (SFC), the extraction efficiency (SFE), or the degree of cleaning (SFBC).

We have initiated experiments to probe solute-fluid interactions at interfaces. Our current model system is amino propyl controlled glass (A-CPG) tagged with a fluorescent dansyl probe. A careful series of labeling experiments (surface amine:probe ratios from 10:1, saturation to 10^{-5}:1) show that there are at least two domain types surrounding the amine residues on A-CPG: (a) a low concentration of amines that are well separated, exhibit low accessibility, and are surrounded by non polar environments and (b) a high concentration of amines that are in close proximity and are highly accessible. Liquid solvent and $scCO_2$ studies reveal tremendous differences in the apparent cybotactic region that surrounds the dansyl probe that depend in a direct way on the amine:probe ratio.

Room temperature ionic liquids (RTILs) are liquids composed entirely of ions that are molten at room temperature. Although there are several classes of RTILs, most share common properties such as a wide electrochemical window, high conductivity/ionic mobility, broad liquid temperature range (~300 °C), negligible vapor pressure, chemical and thermal stability, and the ability to solvate a variety of organic and inorganic species. One key feature of RTILs is that certain bulk properties (e.g., melting point, viscosity, hydrophobicity) can be tailored by varying the nature of the cation and/or anion, allowing one to customize a RTIL for specific needs.

We have focused on asssessing the local environment surround solutes dissolved in $[bmim]^+$ $[PF_6]^-$ as a function of temperature and added CO_2 by using steady-state and time-resolved fluorescence.

Significant achievements: Achievements include: (a) a detailed molecular-level view of oligomer tail-tail and junction point dynamics in pure liquids, CO_2-expanded liquids, and pure $scCO_2$; (b) important insights into the use of probes to study interfaces and probe-probe, probe-surface, probe-surface-liquid, and probe-surface-fluid interactions; and (3) the RTIL solvation dynamics.

Plans for future research on this project: Future work will involve: (a) extensions of the polymer and CPG work to cosolvent-modified fluids, (b) exploration of other surfaces, and (c) sub-picosecond dynamics experiments on a suite of RTILs with a wider range of probe molecules.

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Probing Metal-Ligand Interactions through Actinide-Polyoxometalate Complexes and Room-Temperature Ionic Liquids

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Overall research goals: Our research program seeks an improved understanding of the nature of the atomic-scale interactions between metal atoms/ions and ligands and the changes in them brought about by physical or chemical transformations, with the ultimate objective of controlling their strength and selectivity. Within this broad framework lie two overlapping areas of investigation. In the first, metal ion-selective ligands are designed, synthesized, and characterized. By systematically varying the chemical properties of these ligands and the properties of the metal ions with which they interact, the factors controlling metal-ligand binding can be elucidated. In the second area, the effects of solvation and redox activity on metal-ligand interactions in both conventional and "neoteric" media are explored. In these studies, it is our objective to determine the relative importance of metal-ligand bonding and metal-solvent, ligand-solvent, complex-solvent, and solvent-solvent interactions in influencing metal-ligand and electrochemical equilibria.

Specific objectives for 2002-2003: The absence of detailed information concerning the coordination and redox chemistry of multivalent actinide (*An*) ions in polyoxometalate (POM) complexes has led us to employ a combination of synthetic, electrochemical, spectroscopic, and physical methods to obtain an improved understanding of *An*-O coordination and electrochemistry in aqueous, organic, and ionic solutions of *An*-POM clusters. At the same time, we have undertaken studies designed to elucidate the mechanism of gelation in hydrophilic room-temperature ionic liquids (RTILs) and of metal ion transfer between aqueous solutions and RTILs containing various extractants. Of particular interest in these studies is the influence of RTIL structure on the propensity toward gel formation and of solvent characteristics on the mode of ion transfer.

Significant achievements: Although tetravalent actinide ions are known to be stabilized by the formation of coordination complexes with POMs such as the Wells-Dawson anion, $[P_2W_{17}O_61]^{10-}$, there is little structural information concerning the *An*-O interactions, particularly in solution. Using extended X-ray absorption fine structure (EXAFS) measurements, we have probed the *An*-O coordination environment for the series of clusters $[An(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{n-}$ with An^{4+} and An^{3+}. The average $An^{n+}\text{-}O_8$ distances correlate with their cationic VIII-coordinate ionic radii, consistent with simple charge and size considerations. Thus, the stability of An^{4+} (particularly Am^{4+}) in $[An(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ complexes can be understood in terms of electrostatic interactions between the spherical An^{4+} cations and the anionic POM ligands (1).

Through a combination of extraction studies and EXAFS, nuclear magnetic resonance, and ion chromatographic measurements, we have recently demonstrated that the transfer of strontium ion from aqueous nitrate solution into 1-methyl-3-pentylimidazolium bis[(trifluoromethyl)sulfonyl]imide (a representative IL) containing a neutral extractant (*i.e.*, a crown ether) proceeds via cation-exchange, in contrast to conventional solvents, for which extraction of a strontium nitrato-crown ether complex is observed (2, 3).

In related work, addition of water to 1-decyl-3-methylimidazolium bromide has been shown to result in its spontaneous self-organization and the concomitant formation of a liquid-crystalline gel, thus providing a simple means of preparing a supramolecular assembly comprising a room-temperature ionic liquid (4).

Plans for future research on this project: We will use a combination of synthetic, electroanalytical, spectroscopic, and physical methods to examine the electrochemistry of *An*-POM clusters in aqueous, organic, and ionic solutions, thus revealing the interrelationship between POM framework electroactivity and the bonding and redox behavior of the *An* ions. The synthesis and characterization of *An*-POM clusters with dual redox centers and multielectron activity will afford unique access to knowledge about longstanding issues in correlated electronic interactions as well as insights into the participation of f-electrons in bonding (5).

Our studies of metal ion partitioning into RTILs will be extended to determine the effect of the formation of neutral (rather than cationic) complexes on the mechanism of ion transfer. In addition, we will carry out a systematic examination of the physicochemical properties of IL-based gels and their relationship to IL characteristics.

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Abstract P7-2

Fundamental Studies in Novel Separations

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- Overall research goals: This project brings established capabilities to bear on novel separation systems and complex problems in separations with the aim of improving fundamental understanding and, thereby, increasing efficiency and reducing costs.

Represents only one third of the project (the other two thirds are led by Sheng Dai and Hank Cochran of Chemical Sciences Division of Oak Ridge National Laboratory), this part of the project is focused on

- Investigation of novel separation methodologies
- Study of molecular structures near solid/liquid interfaces through simulations, neutron reflectometry, and measurement of colloidal forces
- Ionic liquids as novel separation media

Specific objectives for 2002-2003: Separations by means of microporous and mesoporous structures are investigated. Studies include molecular distributions near liquid-solid interfaces, forces between colloidal particles, ionic liquids as novel separation media, and field-enhanced separations. Specific subjects are described as follows:

Electrosorption in Nanopores. The surface charge of nanoporous electrically conductive materials can be manipulated by direct application of an electrical potential. The distribution of ions near the electrified surface, also known as the electrical double layer (EDL), can thus be manipulated, leading to the phenomenon of electrosorption. This phenomenon is reversible and can be used in the separation of ions from aqueous solutions, development of supercapacitors for energy storage applications, and development of sensors. Experimental and modeling studies have been undertaken to study electrosorption of ions in nanopores. Experiments based on cyclic voltammetry have shown that nanostructured platinum electrodes with uniform nanochannel structure can be employed to selectively separated anions. In addition, carbon based materials (carbon aerogel) with a wide pore size distribution have been used for electrosorption, and their behavior was explained by considering the distinct behaviors of mesopores and micropores. Micropores (<2 nm) showed a dependence on the scanning rate of cyclic voltammetry. A fast scanning rate gave the fingerprints of mesopores, while a fast scanning rate revealed the synergistic behavior of mesopores and micropores.

An electrical-double-layer model based on the pore-size distribution of the material was developed to predict the electrosorption capacity of nanostructured carbon aerogel. This model, however, that is based on the Gouy-Chapman theory, does not work well at low electrolyte concentration and low surface charge density. Thus, Monte Carlo techniques have been employed to better investigate the EDL formation. Monte Carlo simulations have shown that water molecules play an important role in EDL formation in nanopores because they strongly adsorb on the charged surfaces. Adsorption of ions on the charged surfaces is determined by their hydration radius and the hydration energies. It was also found that the disagreement between the Gouy-Chapman model, the primitive Monte-Carlo model that does not consider the water molecules, and the nonprimitive model that includes water molecules, increases when the pore size is decreased.

Investigation of Metal Ion Adsorption Using Atomic Force Microscopy. Sorption of ions modifies the surface properties of colloidal particles, which are reflected in the interaction force between a particle and another surface. This force is measured in this study by atomic force microscopy (AFM). The sorption of copper ions from aqueous solutions by silica particles is investigated. The effect of metal ion concentration and solution ionic strength on surface forces is studied under transient conditions. Results show that as the metal ion concentration is decreased, charge reversal occurs and a longer period of time is required for the system to reach equilibrium. The ionic strength has no significant effect on sorption kinetics. Furthermore, neither metal concentration nor ionic strength exhibits any effect on sorption equilibria for the experimental conditions used in this study. This reveals that the surface sites of the silica particle are fully occupied by copper ions.

Interaction of Colloidal Spheres Close to a Charged Plate. One of the prominent open questions in colloidal science is the like charge attraction of colloidal particles in confined geometries or close to charged walls. *Larsen and Grier* (1997) observed that the pair potential reaches a minimum for a certain sphere-plate distance. A theoretical explanation of this phenomenon has been attempted by consideration of electrostatic interaction as well as hydrodynamic coupling between the spheres and the plate. In this work, the electrostatic model of *Sader and Chan* (1999) and the hydrodynamic model of *Squires and Brenner* (2000) are discussed and compared with experimental data. The effects of geometrical changes, such as sphere-wall and sphere-sphere separation, as well as the variation in physicochemical parameters, such as the ionic strength and zeta-potential, are analyzed. It is shown that the hydrodynamic coupling is the dominating effect, while the electrostatic influence may be often neglected. Some observations, however, can only be explained by means of a combined electrostatic-hydrodynamic model that is derived in this work. While the hydrodynamic model predicts a monotonically decreasing pair potential for decreasing sphere plate distance, a potential minimum can be computed with the combined model for a certain sphere-to-wall distance as found in the literature.

Significant achievements:

- Separation of ions from aqueous solutions by electrosorption using porous electrodes has been experimentally and theoretically investigated and the behavior of micropores with respect to electrical double layer formation was elucidated.
- Effects of applied electric fields on drop–interface and drop–drop coalescence have been studied and a method of controlling phase inversion in liquid dispersions was devised (Patent # 6,495,617).

Plans for future research on this project:

- Molecular structures near solid/liquid interfaces and under the influence of external fields will be investigated through simulations, neutron reflectometry, and measurements of colloidal forces.

Abstract P7-3

Actinide(III, IV) Phosphine Oxide and Nitrile Complexes

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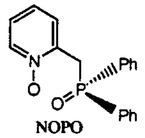
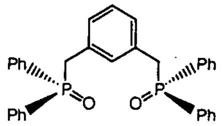
Collaborator: Prof. Robert Paine, Department of Chemistry, University of New Mexico

Overall research goals: Actinide coordination chemistry has generally been studied to accomplish analytical and bulk scale separations. More recently, interest has grown in the chemistry of the early actinides under biological and environmental conditions, for remediating contaminated sites and forecasting environmental impact. Our goal is to develop fundamental actinide chemistry, primarily that of Pu, towards application in both of these broad areas.

Specific Objectives for 2002-2003: Our primary objectives for this year were to prepare new low-valent actinide starting materials and to continue our collaborative study of actinide complexes of mixed pyridine N-oxide and phosphinoxide ligands. 1. Low-valent early actinide nitrile compounds. We previously reported a Pu(III) aquo compound, $[Pu(H_2O)_9][CF_3SO_3]_3$, prepared by the dissolution of Pu metal in triflic acid. Given this preparation of a homoleptic complex and the fact that virtually all nonaqueous An(III) complexes have been prepared through the triodide-tetrahydrofuran complex, we sought to explore the metal oxidation in nonaqueous solvents other than tetrahydrofuran. 2. Actinide phosphine oxide compounds. More directly relevant to lanthanide/actinide separations, we have prepared and are studying Pu complexes of pyridine N-oxide and phosphinoxide ligands. These compounds have been examined as liquid/liquid extraction agents in chloroform, arene, and alkane solvents, and they show favorable extraction performance for Ln(III) and Am(III) ions from concentrated HCl and HNO_3 solutions. The coordination ability of 2,6-bis[(diphenylphosphino)methyl]benzene P,P'-dioxide (*POPO*) to Ln(III) ions has also been tested. Here 2:1 complexes are isolated, with *POPO* acting as a bidentate ligand. We sought to characterize related actinide complexes.


NOPO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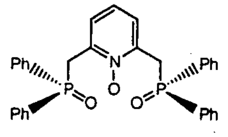
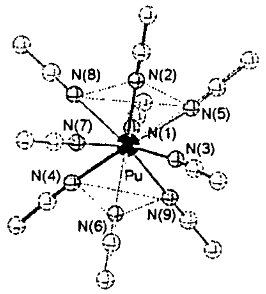

NOPOPO

Significant Achievements: 1. Actinide nitrile compounds. We prepared the first homoleptic acetonitrile actinide complexes, $[Pu(NCMe)_9][PF_6]_3 \cdot MeCN$ (**1**) and $[U(NCMe)_9][I]_3$ (**2**). Complex **1** is prepared by treating an acetonitrile suspension of ^{239}Pu metal turnings under argon atmosphere with three equivalents of either $AgPF_6$ or $TlPF_6$. The acetonitrile solution turns blue as Pu metal dissolves and silver or thallium metal precipitates. Filtration of the solution followed by evaporation results the blue crystalline $[Pu(NCMe)_9][PF_6]_3 \cdot MeCN$ in 80% isolated yield. The crystal structure of **1** shows a $[Pu(NCMe)_9]^{3+}$ cation surrounded by three non-coordinating hexafluorophosphate anions. The central Pu atom is bound by nine acetonitrile nitrogen atoms to form a distorted tricapped trigonal prism. Attempts to isolate the uranium analogue of **1** by the same method were unsuccessful. However, dissolution of $UI_3(THF)_4$ in acetonitrile followed by cooling to –35°C yields



dark green crystals of the target homoleptic U(III) acetonitrile complex, $[U(NCMe)_9][I]_3$. The crystals of **2**, unlike the Pu analog, are thermally unstable and rapidly decompose at room temperature to yield an uncharacterized black residue. When the oxidation of uranium metal was carried out in benzonitrile, the mononuclear U(IV) product $UI_4(NCPh)_4$ is obtained.

2. Actinide phosphine oxide compounds. The *NOPOPO* ligand is sterically very demanding, but always behaves as a tridentate ligand. In contrast, the *POPO* ligand has approximately the same steric bulk as *NOPOPO*, but occupies one less coordination site. The *POPO* ligand can form 2:1 complexes with Ln(III) ions and structures for $[(\mathit{POPO})_2(Ln)(NO_3)_2]\cdot 0.5MeOH$ have been reported. We attempted to prepare a 2:1 ligand to metal complex of *POPO* with Pu(IV). We discovered that treatment of Pu (IV) in dilute acid with two or more equivalents of *POPO* in methanol produced intractable products. However, slight modifications to the reaction allowed us to isolate and characterize two distinct 1:1, POPO:Pu(IV) products. The first was obtained when the residue from a 2:1 reaction of *POPO* and Pu(IV) nitrate was dissolved in chloroform. Solvent evaporation produced orange crystals of $(\mathit{POPO})Pu(NO_3)_2Cl_2$ and its structure of was determined.

The second product was prepared by adding excess sodium hydroxide to a solution of excess *POPO* in methanol spiked with Pu (IV) nitrate solution. Sodium hydroxide was added in an attempt to sequester nitrate and encourage coordination of a second *POPO* ligand to the Pu(IV) center, but generates NaOMe instead. The methoxide ion effectively competes with nitrate for the Pu center and solvent evaporation provides crystalline $(\mathit{POPO})Pu(NO_3)_3(OMe)$ as the only product. This result is not unexpected given the oxophilic nature of Pu(IV) and nucleophilicity of methoxide. However, it is surprising that coordination of two methoxide units is not observed especially when the synthesis of the dichloride product is considered.

Plans for future research on this project: 1) We have begun studying Pu(III) complexes of multidentate amine ligands. We have structurally characterized the product formed between trispyrazine amine and $PuI_3(MeCN)_4$ and found an eight-coordinate Pu complex containing the tripodal amine, three iodides and an acetonitrile. The Pu(III) has M-N(amine) and M-N(py) distances of 2.618(6)Å and 2.756Å(av), respectively, compared with 2.668(2) and 2.641Å for a similar Nd(III) complex. Surprisingly, the relative distances to the amine and pyrazine nitrogens are reversed for the two metal ions. This suggests bonding differences for the similarly sized 4f and 5f ions, which we would like to explore further. 2) In our continuing collaboration with Prof. Robert Paine's program, additional Pu(III,IV) and perhaps Am(III) phosphine oxide complexes will be synthesized and characterized. For example, complexes of the benzene analog of the pyridine NOPOPO ligand, where there is no longer an N-oxide group present, will be studied. 3) Additional types of 'soft' ligands will be investigated. For example, several thiolate and thionyl ligands, such as cyanex, are being considered in separation schemes. We propose to structurally characterize light actinide complexes with these non-traditional ligands.

Publications from this project in 2002-2003:

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Abstract P7-4

Reaction Chemistry in Supercritical Fluid Solutions

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Currently, organometallic investigations at PNNL are directed towards the identification of homogeneous reaction rates and intermediates addressable by NMR. The role solvent density has on controlling reaction end-products, intermediate species, and catalyst resting states is being investigated. *In situ* high-pressure NMR investigations of homogenous catalytic reactions in liquid and supercritical CO_2 are useful in identifying reaction intermediates and determining observed reaction rates. The hydroformylation reaction of ethylene in liquid CO_2 using $Rh(CO)_2acac$ as the catalyst precursor and $(p\text{-}CF_3C_6H_4)_3P$, tris(*p*-trifluoromethylphenyl)phosphine, as the ligand under different thermodynamic conditions (T = 10°C and 23°C, $P_{CO} = P_{H2} = 10 - 15$ bar, $P_{C2H4} = 10 - 15$ bar, total pressure in CO_2 is 207 bar) was investigated. ^1H NMR was used to monitor the reaction progress of the hydroformylation of ethylene with the rhodium catalyst under select conditions of temperature and CO_2 solvent pressure. Potential resting states of the rhodium catalyst were investigated by $^{31}P\{^1H\}$ NMR. This is the first description of a rhodium catalyzed hydroformylation reaction in liquid CO_2 monitored *in situ* by high pressure NMR.[1] The proposed $HRhCO((p\text{-}CF_3C_6H_4)_3P)_2(\eta^2\text{-}C_2H_4)$ intermediate was identified directly *in situ* for the first time. This set of experiments demonstrates that high-pressure NMR can be used to observe *in situ* a reaction in the supercritical CO_2 solvent between highly soluble gaseous reactants and an organometallic catalyst. This technique is useful for determining reaction intermediates and describing the turn-over frequency of reactions in sub- and supercritical fluids. At both 10°C and 23°C, the propanal formation is linear as a function of time. The turn-over frequencies for the formation of the aldehyde ([mol aldehyde][mol Rh]$^{-1}$ h^{-1}) are ~5 [mol aldehyde][mol Rh]$^{-1}$ h^{-1} and ~34 [mol aldehyde][mol Rh]$^{-1}$ h^{-1} at 10°C and 23°C, respectively.

Ionic liquids are currently being used in combination with supercritical fluids for catalytic reactions due to the ease of extraction of reaction products by fluids from such bi-phasic systems. The use of ionic liquids in catalytic processes with organic liquids using either sub or supercritical CO_2 to alter the solution phase behavior begs the question of potential chemistries in these solvent systems. Current investigations are focused on a simple salt hydrate, tetramethylammonium fluoride tetrahydrate, $[(CH_3)_4N]F\bullet 4H_2O$, as a neat melt and dissolved in methanol in contact with supercritical and subcritical CO_2. This hydrate is proposed as a simulant for more complex ionic liquids, to investigate any potential secondary reaction chemistry in these solvent systems with carbon dioxide. Prior work in the literature has described the formation of bicarbonate using this salt hydrate as a melt in the presence of CO_2 as shown in reaction 1.

$$2\,F^-\bullet nH_2O + CO_2 \rightarrow HCO_3^- + HF_2^-\bullet(2n-1)H_2O \qquad (1)$$

The presence of the proposed HF_2^- species could impact the reaction chemistry in solution. Lewis acid/base interactions between CO_2 and the anion in the ionic liquid, i.e., $[BF_4]^-$ and $[PF_6]^-$ has been suggested to play a role in the solubility of CO_2 into the ionic liquid. The fluoride ion in the presence of associated water in $[(CH_3)_4N]F \bullet 4H_2O$ should be a powerful base and could account for the reported large sorptive capacity for CO_2. Tetramethylammonium fluoride tetrahydrate should lend itself to the investigation of any Lewis acid/base chemistry in ionic liquid solvent systems or fluoride ion chemistry caused by the hydrolysis of the anions, such as $[BF_4]^-$ and $[PF_6]^-$ in solution. Evidence is presented for the formation of methylcarbonate, $CH_3O(C{=}O)O^-$, and fluoromethane, CH_3F, in solution when the salt hydrate is in contact with methanol and CO_2. This secondary reaction chemistry between CO_2 and an organic modifier (methanol and ethanol) with $[(CH_3)_4N]F \bullet 4H_2O$, under sub or supercritical conditions is investigated by *in situ* ^1H, ^{19}F and $^{13}C\{^1H\}$ high-pressure NMR spectroscopy.[2]

In the future, time-resolved FTIR studies of the kinetics of free radical reactions in supercritical fluids will be initiated. The goal of these investigations is to detail on a molecular level the effect of radical structure and solvent cage on the reaction kinetics of free radicals in supercritical fluid solutions. Preliminary studies have involved the investigation of the kinetics of radical recombination in supercritical CO_2 and Xe as a function of pressure and temperature for comparison with the same reaction in liquid solvents. The wide range of physical conditions available with supercritical fluids allows one to investigate the effect of viscosity and solvent cage dynamics without altering the chemical interactions between the radical and the solvent. The structural information available from FTIR allows a definitive identification of the reaction pathways and dynamics in compressible fluids. Organometallic compounds provide the opportunity to investigate hindered rotation about metal/ligand bonds and ligand exchange as a function of pressure and temperature. These investigations could lead to a more fundamental understanding of the fluid solvent cage about the organometallic molecule. Some preliminary results will be presented.

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Abstract P7-5

CHEMICAL THERMODYNAMICS OF ACTINIDES IN SOLUTION UNDER NON-CONVENTIONAL CONDITIONS

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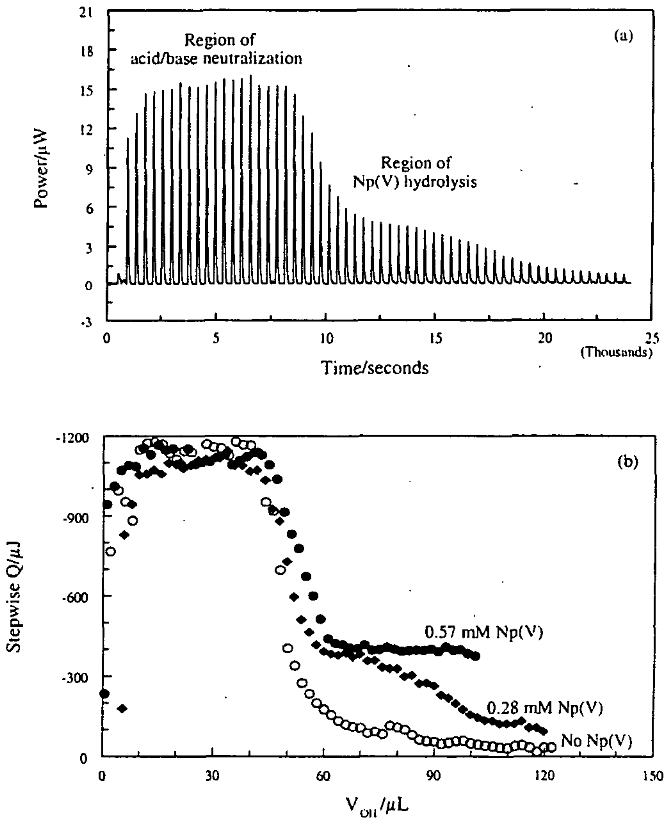
Overall Research Goals: The goal of this research program is to improve the understanding of fundamental principles governing the chemical behavior of actinides in solution under non-conventional conditions, including elevated temperatures, high ionic strength systems, neutral to alkaline solutions, and non-aqueous solutions.

Specific objectives for 2002-2003: 1) to extend the studies to other ligands with different denticiy and donar atoms so as to test the validity of the electrostatic model in interpreting the temperature effect; 2) to extend the studies to transuranic elements.

Significant achievements: Both the isothermal and isoperibol calorimeters have been in continuous operation for thermodynamic studies of actinide coordination with organic ligands and actinide hydrolysis from 10 °C to 85 °C.[1-3] Work on U(VI) hydrolysis has been completed. Despite that the hydrolysis of U(VI) has been studied by numerous researchers for many years, our work provides the first set of enthalpy data on U(VI) hydrolysis directly measured at variable temperatures.[4] Calorimetry on Np(V) hydrolysis is under way. The microcalorimeter allows the use of only 0.05 – 0.1 mg Np-237 (i.e., 0.035



– 0.07 μCi) for each titration. The experiments at 25 – 85 °C have been completed. A calorimetric titration thermogram for Np(V) is shown in Fig.a. Integration of the peaks results in stepwise heat that is generated after each addition of the titrant (Fig.b). Processing of these data is underway. When completed, this study will provide an important piece of fundamental information on Np(V) hydrolysis that is still missing in the most recent thermodynamic data base on neptunium and plutonium. It is expected that the variable temperature data on U(VI) and Np(V) hydrolysis will significantly improve the predictability on actinide hydrolysis and migration at higher temperatures.

Plans for future research on this project: 1) Continue the studies of actinide coordination (including hydrolysis) at elevated temperatures, with emphasis on transuranic elements, particularly neptunium (V) and plutonium (IV/VI). 2) Continue the collaboration with the research group in University of Padova, Italy, with emphasis on studies of the change of solvent structure and properties with temperature and its effect on actinide complexation. 3) Collaborate with Raymond group at UC Berkeley. The unique capability of the calorimetry laboratory at LBNL will help acquire important thermodynamic parameters for the metal/ligand systems that have implications in areas such as the formation of nanostructures, catalysis inside supramolecular clusters and separations processes.

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3. Bismondo, P. Di Bernardo, P. Zanonato, J. Jiang, L. Rao, Complexation of thorium(IV) with 2-furoic acid and 2-thenoic acid in aqueous solution, *J. Chem. Soc., Dalton Trans.*, 2003, 469-474. LBNL-51619
4. L. Rao, A. Yu. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo, The effect of temperature on the complexation of uranium(VI) and samarium(III) with oxydiacetic acid, Lawrence Berkeley National Laboratory Technical Report, January 2003. LBNL-52011

Multilayered Polyelectrolyte Films as Highly Selective Nanofiltration Membranes

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Overall research goals: The objective of this project is to control and understand the formation and selectivity of ultrathin, multilayered polyelectrolyte membranes (MPMs). Such membranes are attractive because their minimal thickness allows high fluxes, and control over polyelectrolyte composition and structure provides a means for developing high selectivities. While we are gaining an understanding of the mechanisms of selective transport through MPMs, we are creating remarkably selective systems for nanofiltration of salts and sugars. Exploitation of the versatility of polyelectrolyte deposition also aims at development of catalytic membranes.

Specific objectives for 2002-2003: Goals for the current funding year include determination of the relative contributions of charge and size to ion-transport selectivity, examination of selectivities in nanofiltration systems, investigation of the properties of MPMs containing dendrimers as polycations, and development of nanocatalysts in polyelectrolyte films. Only the first two objectives will be discussed herein.

Significant achievements: One highlight of our recent work is the demonstration of large size-based selectivities in diffusion dialysis with MPMs. To avoid any influence of charge on selectivity, we performed transport experiments using a series of neutral, hydrophilic analytes with Stokes diameters ranging from 1.0 to 9.4 nm. Remarkably, even simple polyelectrolyte membranes such as poly(styrene sulfonate)/poly(allylamine hydrochloride) (PSS/PAH) show glucose/sucrose selectivities of 150. Glycerol/glucose selectivities are about 8. The high selectivity of glucose over sucrose suggests that the molecular weight cutoff of these membranes will likely be somewhere between 180 (the molecular mass of glucose) and 342 (the molecular mass of sucrose).

To attain selectivity among smaller molecules, we capped films with poly(acrylic acid) (PAA)/PAH because PAA packs more densely than PSS. Using these membranes, we achieved glycerol/glucose selectivities of 75. For neutral molecules similar in size to ions (methanol and glycerol), however, selectivities are significantly lower. Methanol/glycerol selectivity is only 3.5 for a PSS/PAH membrane capped with PAA/PAH, and for pure PSS/PAH membranes, this selectivity is only 2. Thus, the selectivity of ion-transport in MPMs probably contains both size and charge contributions.

A second focus of our research is the development of highly selective nanofiltration (NF) membranes. The moderate pressures (~70 psi) in NF allow purification of water and provide higher ion-fluxes than those in diffusion dialysis. For a 4.5-bilayer PSS/PAH membrane with a top layer of PSS that was deposited from a solution containing 2.5 M $MnCl_2$, Cl^-/SO_4^{2-} NF selectivity is about 30. The presence of the large excess of $MnCl_2$ during deposition of the top layer increases surface charge and enhances NF selectivity approximately 5-fold relative to films prepared in the presence of 0.5 M $MnCl_2$. Remarkably, flux through PSS/PAH membranes (1.8 m^3/m^2/day) is about twice that through commercial NF membranes. Changing the surface layer from PSS to poly(acrylic acid) results in Cl^-/SO_4^{2-} NF selectivities as high as 80, but water flux decreases by a factor of two.

Interestingly, Cl^-/SO_4^{2-} selectivities calculated from single-salt measurements are as much as 4-fold lower than those determined with mixtures of salts. This difference likely stems from diffusion potentials. In NF with only Na_2SO_4, a large diffusion potential develops because the mobility and/or concentration of Na^+ in the membrane is much greater than that of SO_4^{2-}. (In the membrane, differences in cation to anion ratios relative to salt stoichiometry result from fixed charge.) The diffusion potential in solutions of Na_2SO_4 enhances the transport of SO_4^{2-}. For solutions containing only NaCl, diffusion potentials are minimal because the mobilities and concentrations of Na^+ and Cl^- are similar. In solutions containing both Na_2SO_4 and NaCl, however, the concentration of Na^+ in the feed solution is greater than the concentration of Cl^-, and thus diffusive flux of Na^+ should be greater than that of Cl^-. This creates a diffusion potential that is smaller than that in Na_2SO_4 solutions, but larger than that in NaCl solutions. Thus, relative to single-salt solutions, the diffusion potential in mixed solutions causes a decrease in Cl^- rejection and an increase in SO_4^{2-} rejection, yielding enhanced selectivities. By employing high Na_2SO_4 concentrations in mixed solutions, we can actually achieve Cl^- concentrations that are higher in the permeate than in the feed.

Plans for future research on this project: MPMs are very promising candidates for selective nanofiltration of ions, and diffusion dialysis experiments suggest that these membranes are also attractive for size-based separation of neutral molecules. Thus, future work will examine selective nanofiltration of sugars and small alcohols, as well as separation of large ions having the same charge, but somewhat different sizes. Additionally, separation of sugars from salts should be a natural application of MPMs. We will also investigate fundamental fouling properties of MPMs, because fouling could greatly reduce flux and limit the utility of these systems. Finally, we will study the formation of polyelectrolyte films on porous polymeric supports. Our previous studies involved porous alumina substrates, but these materials are not practical from a cost and fragility standpoint.

Publications from this project in 2002-2003:

1. D.M. Sullivan and M.L. Bruening, "Ultrathin, Gas-selective Polyimide Membranes Prepared from Multilayer Polyelectrolyte Films", *Chem. Mater.*, **15**, 281-287 (2003).

2. B.Y. Kim and M.L. Bruening, "pH-Dependent Growth and Morphology of Multilayer Dendrimer/Poly(acrylic acid) Films", *Langmuir*, **19**, 94-99 (2003).

3. M.L. Bruening, "Controlling the Ion-Permeability of Layered Polyelectrolyte Films and Membranes", in *Multilayer Thin Films*, G. Decher and J. B. Schlenoff, eds., Wiley-VCH, Weinheim, Germany, pp. 495-510 (2003).

4. M.L. Bruening and D.M. Sullivan, "Enhancing the Ion-Transport Selectivity of Multilayer Polyelectrolyte Membranes", *Chem. Eur. J.*, **8**, 3832-3837 (2002).

Abstract P7-7

Gas-Phase Actinide Ion Chemistry: Thermochemistry of Actinide Oxide Molecules

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Introduction

The goal of this project is to enhance fundamental understanding of actinide chemistry in the context of actinide electronic configurations and energetics, and particularly the role of the 5f electrons. The results are additionally important for developing technological applications, and understanding the science that underlies the behavior of actinides.

Organometallic reactivity illustrates the role of actinide electronic structures and energetics in gas-phase ion chemistry. We have examined hydrocarbon activation by ions of ten actinides, Th through Es.[1] The An^+ promotion energies from the ground state to the prepared "divalent" state, $[Rn]5f^{n-2}6d7s$, are shown in Figure 1. Hydrocarbon activation efficiency is greatest for $Pa^+/U^+/Np^+$, intermediate for $Pu^+/Cm^+/Bk^+$, and minimal for $Am^+/Cf^+/Es^+$. The reactivity markedly decreases with increasing promotion energy, indicating that the 5f electrons for An^+ heavier than Np^+ are chemically inert in organometallic bond activation. Results for hydrocarbon activation by PaO^+[2] and UO^+[3] have provided evidence for 5f participation for lighter actinides.

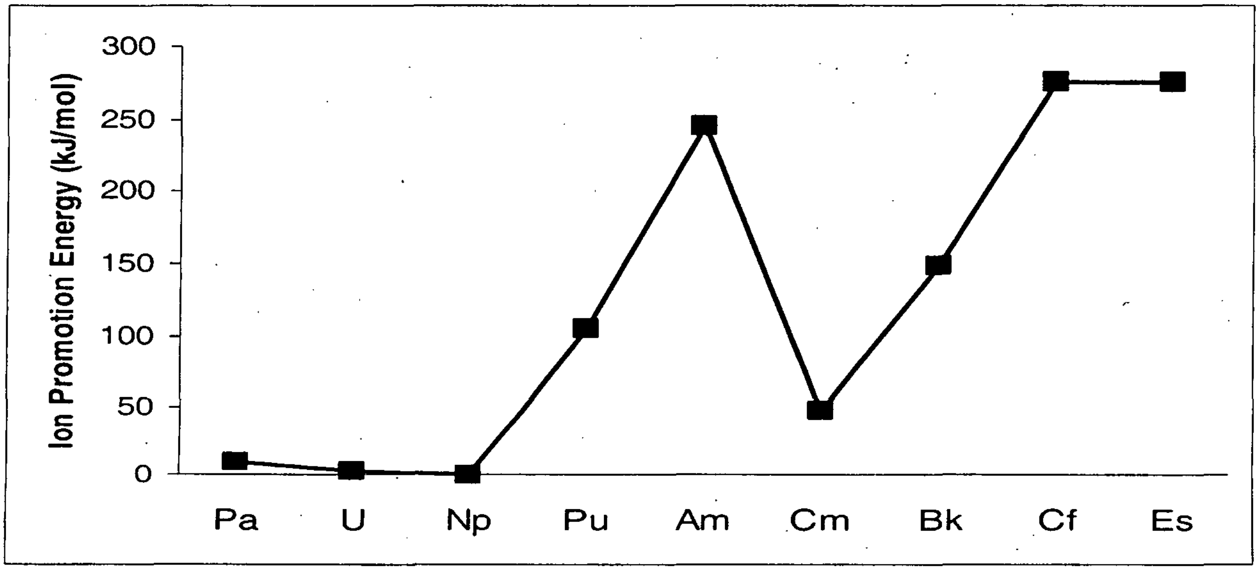

Figure 1 – An^+ promotion energies from the ground to the $5f^{n-2}6d7s$ configuration.

Thermochemistry of Transuranium Actinide Oxide Molecules

In collaboration with ITN, we are studying actinide ion chemistry using FTICR-MS with an initial emphasis on thermochemistry of actinide oxides.[4] Bond dissociation energies (BDEs) are determined by reactions of An^+ and AnO^+ with oxidants, and ionization energies (IEs) are determined by charge exchange reactions. Results for Np and Pu are summarized in Table 1. For neptunium monoxide the results are in accord with the literature; these are the first such studies for neptunium dioxide. Our results suggest that IE(NpO_2) $\geq$ 6 eV, in contrast to the anomalously low literature value of 5.0 eV. Our lower limit for BDE(Pu^+-O) is in accord with one of two conflicting literature values, and we obtained an IE(PuO) that is significantly smaller than the reported value of 6.6 eV. For plutonium dioxide we conclude that BDE(OPu$^+$-O) is twice as large as the literature value of 261 kJ/mol, and that IE(PuO_2) is 3 eV lower than the reported value of 10.1 eV. The erroneous literature values for plutonium dioxide were incompatible with systematic trends and we have obtained reliable values that are consistent with predictions.

Table 1 – Measured and derived thermodynamic quantities*

	Neptunium	**Plutonium**
BDE(An$^+$-O)	**≥752**	**≥632**
IE(AnO)	**5.7±0.1**	**5.8±0.2**
BDE(An-O)	**≥700**	**≥610**
BDE(OAn$^+$-O)	**580±70**	**520±20**
IE((AnO_2)	**(≥6)**	**7.03±0.12**
BDE(OAn-O)	**(≥600)**	**640±30**

*Bond dissociation energies are in kJ/mol; ionization energies are in eV.

Future Plans

We will continue to examine new aspects gas-phase actinide ion chemistry, and plan to extend this line of inquiry to Ac and Fm. Trapped ion mass spectrometry will provide more quantitative and detailed information on gas-phase organoactinide ion chemistry. Measuring reaction rates of An$^+$ and AnO$^+$ with hydrocarbons will distinguish between ions with similar promotion energies, such as Am$^+$ and Cf$^+$ Discerning the role of the 5f electrons in molecular chemistry remains a central goal and will be addressed by studying such phenomena as the onset of activation of alkanes by An$^+$ as a function of carbon chain length.. In view of the remarkable reactivity of Pa$^+$ with alkenes[2] it is important to more closely examine the chemistry of this first actinide ion to have 5f electrons in its ground state. Other reaction substrates of particular interest for elucidating systematic variations within the actinide series include substituted benzenes (e.g., phenol) and sulfur hexafluoride.

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Abstract P7-8

Hierarchical Synthesis of Materials for Separation

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Hierarchical structures can be found in nature from the macroscopic level to the microscopic level. Biomaterials are selectively self-organized from molecular- to macro-length scales, with organized units of subassemblies that are generated to serve biological purposes. They are smartly chosen from a multitude of options. Recently, research has been initiated to mimic biomineralization processes and chemically produce hierarchical structures.[1-7] Notably, the research groups of Ozin and Mann have established a morphosynthesis approach to inorganic and hybrid materials with complex forms.[1-3] Three methodologies are predominantly used in their material synthesis. First, complex macroscopic morphological forms can be produced by fluctuating chemical processes involving local perturbations in the fluid-solid interface during mineralization. Secondly, organic assemblies such as micelles are used as scaffold-like templates to direct mineralization along, around, and between the organic-inorganic interfaces. Thirdly, patterned organic compartments (vesicles) are used to shape biomaterials through "organized reaction fields."

We have recently introduced a facile approach to the production of hierarchical microstructure and mesostructures.[8] The essence of our new methodology is the combination of two powerful imprinting techniques at different scales: (i) molecular imprinting and (ii) micelle templating synthesis. For example, surfactant micelles and metal ions both can act as templates in this *hierarchical imprinting synthesis*. The removal of these two templates results in the formation of different-sized imprints within the templated matrix, each with a specific function. On the microporous level, removal of the metal ion from the corresponding complex leaves cavities (1-3 Δ) that exhibit ionic recognition. These pores give the sorbent enhanced selectivity for the given ion. On the mesoporous level, removal of the surfactant micelles results in the formation of relatively large, cylindrical pores (diameters of 25-40 Δ) that give the matrix an overall porosity, including large surface areas and excellent metal-ion transport kinetics. These hierarchical materials may find important applications as smart sorbents for environmental cleanups. The motivation for synthesizing hierarchical materials with microscopic, mesoscopic, and macroscopic forms centers around the synergistic importance of stereochemistry, pore size, and surface area in determining such properties as flow and transport phenomena, capacity, and selectivity in separation efficiency. The general concept provides a rational way to synthesize hierarchical materials for separation applications.

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Abstract P7-9

Synthetic and Structural Studies of Organoactinides and Other Compounds

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Overall Research Goals: Extensive studies are underway to prepare organometallic and coordination compounds of the *f*-block elements that show the differences and similarities among the *f*-elements and between the *f*- and d-transition elements so that a detailed pattern of their chemistry can be delineated. The emphasis of these studies is to prepare new types of compounds that illustrate new bonding and reaction chemistry concepts, including mechanistic ones. The purpose of the mechanistic studies is to aid our understanding of molecular chemistry that occurs in solution so that approaches can be developed to exploit and control kinetic lability of the *f*-block metal compounds. An additional goal is to study *f*-element compounds in usual oxidation states (the divalent lanthanides and the tri- and pentavalent actinides), and to study their bonding with nontraditional ligands, and their reaction with organic and inorganic molecules.

Specific Objectives of 2002-2003: The synthesis and characterization of the metallocenes of cerium of the type $Cp_2'CeX$, where Cp' is the 1,3,4-tri-t-butylcyclopentadienyl ligand and X is hydride or fluoride, is the most important accomplishment last year. Both of these metallocenes are monomeric in the solid state and in solution, an unusual physical property of the metallocene hydrides and fluorides of the trivalent *f*-block metals. The low coordination number is the result of using the sterically bulky cyclopentadienyl ligand that prevents the monomers from increasing their coordination number by association. The successful synthesis of these monomeric derivatives provides the opportunity to study the intrinsic thermodynamic and kinetic factors, such as relative bond strength and rates of reactions in solution, and how these parameters change as a periodic property. The synthesis of the hydride and fluoride results from the same starting material, $Cp_2'CeCH_2Ph$, which is also monomeric in the solid state and solution. Addition of dihydrogen to $Cp_2'CeCH_2Ph$ yields $Cp_2'CeH$ and toluene; addition of $BF_3(OEt_2)$ to the benzyl yields $Cp_2'CeF$ and $PhCH_2BF_2$. A more interesting synthesis of $Cp_2'CeF$ is the reaction of $Cp_2'CeH$ with C_6F_6, which yields $Cp_2'CeF$, $Cp_2'Ce(C_6F_5)$ and H_2, therefore the net reaction involves the intermolecular activation of a C-F bond.

Exploration of the reaction chemistry of the metallocene hydride and alkyls of cerium as well as extension of these routes to the preparation of the uranium analogues will continue. The reaction of the hydrides with molecules such as carbon monoxide will be studied with the goal of preparing structural models for the industrially important processes of CO reduction. In addition, reactions with fluorocarbon molecules will be systematically explored since this reaction will be useful in understanding how to convert fluorocarbons to hydrocarbons, an environmentally useful process. These reactions will also show the differences between the 4f and 5f block metallocenes in the same oxidation state.

Significant Achievements: Preparation of molecules or discovering reactions that change the way chemists think about *f*-element compounds continues to be our goal. Molecules such as $[(Me_3Si)_2N]_3UH$, the phosphine adduct $(Me_2PCH_2CH_2PMe_2)_2UMe_4$, $Cp_3U(CO)$, and $Cp_3U = NR$ are in this category. The oxidative elimination of dihydrogen from $Cp_4U_2(OH)_2$ to yield $Cp_4U_2(O)_2$ and dihydrogen is such a reaction..

Plans for Future Research on this Project: The research program will focus on exploring the reaction chemistry of the metallocenes $Cp_2'U$ (bipy) and its cerium analogue. The focus of these studies will to explore the synthetic utility of the uranium metallocene to prepare an unknown functional group organoactinide chemistry, the carbene $Cp_2'U(CR_2)$. The synthetic strategy of using bulky substituents the cyclopentadienyl ring system will be extended to a less electron rich, but sterically bulk trimethylsilyl group, that is, the 1,3,4-trimethylsilyl-cyclopentadienyl anion. This ligand will be le electron donating and thus the hypothetical divalent uranium in $Cp_2'U$ (bipy) will be less reducing.

We plan to concentrate on Yb-based systems as a complement to the previously published ceroce work. We will begin this project by establishing (or not) strongly correlated behavior in an Yb-base system. Our leading candidate is the molecule $(Me_5C_5)_2Yb$(2,2'-bipyridyl), abbreviated Cp_2^*Yb(bipy Although this system should be a simple donor-acceptor adduct of $Cp_2^*Yb(II)$, which has a close sphere electronic configuration and therefore is diamagnetic, the bipyridyl adduct is rough paramagnetic over the temperature range 5-300 K, where the effective moment ranges from 0.5 to 2 μB, and the plot of $1/\chi$ vs. T is non-linear, i.e., Curie-Weiss behavior is not observed. The effecti magnetic moment is considerably lower that expected from isolated Yb(III) paramagnets, which a found in the range of 3.8-4.5 μB. Clearly, the ytterbium center is not Yb(II). Conversely, the Yb(II representation is also inaccurate even if there is strong antiferromagnetic coupling between the two sp carriers because of the lack of observed Curie-Weiss behavior. These issues will be explored in futu years.

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Abstract only Abstract P7-10

Molecular Containers with Exquisite Ion Selectivity

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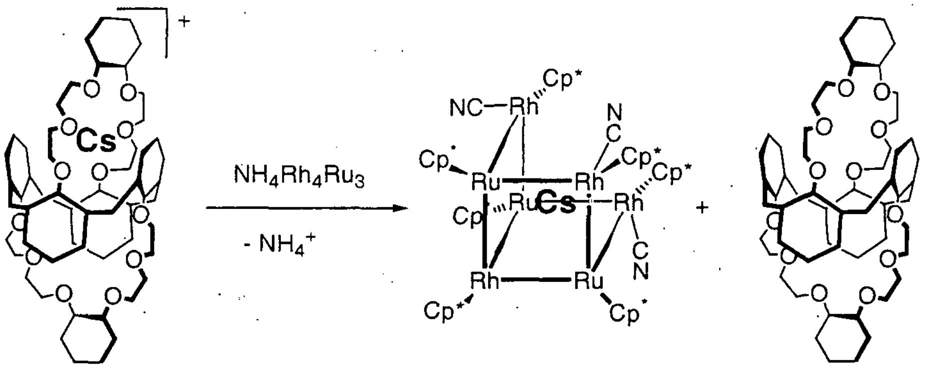
Overall research goals: Develop new hybrid organometallic-inorganic systems for addressing energy-related problems, examples of current or recent themes include fossil fuel desulfurization, hydrogen production, and radionuclide sequestration

Specific objectives for 2002-2003: Investigate the synthesis and ion binding properties of molecular containers through kinetics and structure-function correlations.

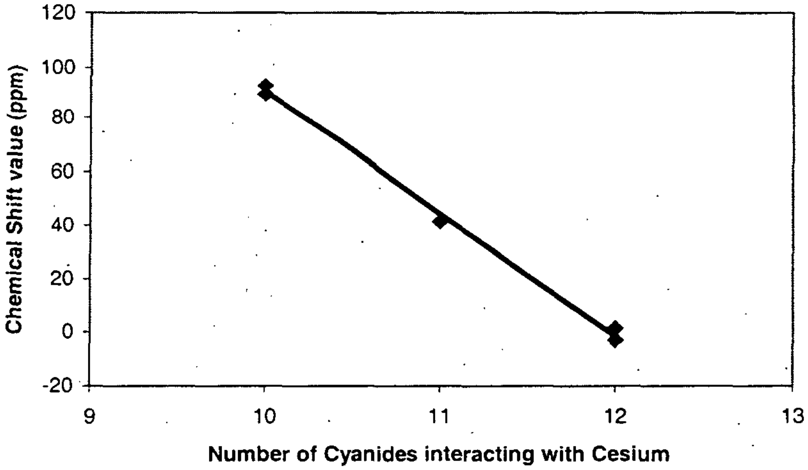
Abstract: Molecular containers are the smallest possible agents for sensing, sorting, and sequestering ions and molecules. Molecular cages based on transition metal vertices often easily self-assemble, and those with inorganic frameworks are of special interest because their rigidity, uncommon in organic ligands, could give rise to highly selective host-guest behavior. Molecular and solid-state Prussian Blue analogues are known to sequester cations, Cs^+ in particular. We are interested in synthesizing new classes of ion receptors that provide fresh insights into the design rules for selective ion complexation.

The empty molecular box $[CpCo(CN)_3]_4[Cp^*Ru]_4$ (**Co_4Ru_4**) was synthesized via the $EtNH_3^+$-templated condensation of $[CpCo(CN)_3]^-$ and $[Cp^*Ru(NCMe)_3]^+$ ($Cp = C_5H_5$, $Cp^* = C_5Me_5$). The size selectivity of **Co_4Ru_4** is highlighted by comparison of the van der Waals volumes of $MeNH_3^+$ (43 Å^3), which binds in the box, vs. $EtNH_3^+$ (60 Å^3), which does not. **Co_4Ru_4** also binds K^+, Rb^+, Cs^+, Tl^+, NH_4^+, and $N_2H_5^+$ but not the smaller Na^+ ($r_{ionic} = 1.16$ Å) or divalent cations. K^+ inserts more rapidly into **Co_4Ru_4**, but Cs^+ is thermodynamically preferred with selectivity >100. Ion insertion into the cage occurs through $Co_2Ru_2(CN)_4$ "windows". Cs^+-for-K^+ ion exchange of **$K{\sqsubset}Co_4Ru_4^+$** into **$Cs{\sqsubset}Co_4Ru_4^+$** is dissociative, whereby the rate limiting step is loss of K^+. The kinetic model for this two-step process was formulated in collaboration with Espenson (Ames Laboratory) and tested vs. various $[Cs^+]_0$. Kinetic measurements allow us to estimate $K_{Cs} > 10^{10}$. Consistent with the slow ion exchange rates, cage-encapsulated guests are chemically shielded from the bulk solution, as demonstrated by isotope exchange experiments.

Whereas the Cs/K selectivities are high and the Cs^+ affinities are high for the boxes, the ion exchange rates are slow. We are addressing this design flaw through studies on "defect boxes", which have more open structures while exhibiting good K/Cs selectivities. The reaction of $[Cp^*Ru(NCMe)_3]^+$ and $[Cp^*Rh(CN)_3]^-$ in the presence of M^+ (M = Cs, NH_4) produces the "defect boxes" $\{M{\sqsubset}[Cp^*Rh(CN)_3]_4[Cp^*Ru]_3$ (**$M{\sqsubset}Rh_4Ru_3$**). The affinity of **$NH_4{\sqsubset}Rh_4Ru_3$** for Cs^+ was tested in a competition experiment against calix[4]arene-bis(benzocrown-6) (**BC6B**), a representative high-affinity Cs-selective ligands. Treatment of a MeCN solution of $[Cs(BC6B)]^+$ with one equiv of **$NH_4{\sqsubset}Rh_4Ru_3$**, results in quantitative conversion to **$Cs{\sqsubset}Rh_4Ru_3$**, see eq:



Cs^+/K^+ and Cs^+/Na^+ selectivities for the boxes and defect derivatives appear to be quite high. The Cs^+---cage interactions can be analyzed by ^{133}Cs NMR spectroscopy (see Figure), which provides a indicator of the number of CN ligands bound to Cs^+.



Significant achievements: Characterization of structurally novel complexants with probably the highest known affinities for Cs^+.

Plans for future research on this project: Develop cages that combine high ion selectivity, high Cs^+ affinity, and high ion-exchange rates. Develop ionophilic cages that feature redox-active centers to demonstrate the concept of electro-release of guest ions.

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The Electronic Structure of Heavy Element Complexes

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Overall research goals: The overarching goal of our research is to use quantum chemical calculations to increase the understanding of the electronic structure of heavy-element systems. Our group has strengths in inorganic chemistry, electronic structure theory, and applications of supercomputing, and we believe that our most important function in the heavy element community is to provide theoretical results and explanations that are significant to experimental chemists in the field. Therefore, we have put our highest priority on obtaining experimentally relevant theoretical results for the heavy-element community. The focus of the research in the past year has been on obtaining an increased understanding of the structure and bonding in small- and medium-sized actinide complexes.

Specific objectives for 2002-2003: The major effort on this project was driven by our collaborative effort with the experimental group of Professor Lester Andrews of the University of Virginia. We have been collaborating with Andrews and coworkers since 1998 in the chemistry of small actinide-containing molecules that are produced in laser-ablation matrix-isolation experiments. In 1999 we published a combined experimental and theoretical study of the products of the reaction of laser-ablated uranium atoms with carbon monoxide. One of the prominent products of this reaction is the triatomic molecule CUO, a neutral molecule that is isoelectronic with the uranyl ion, UO_2^{2+}. The initial experiments on CUO were carried out in a host of solid neon, and we were able to model the molecule successfully as an isolated molecule. Like UO_2^{2+}, we found that CUO would be a linear closed-shell molecule corresponding to uranium in the +6 oxidation state. In late 2001, we used a combined theoretical and experimental approach to discover a remarkable phenomenon about CUO: When an Ar host is used instead of Ne, there is clear evidence for direct interactions between the U atom of CUO and the Ar atoms of the supposedly-innocent matrix. The interactions, which correspond to bond energies of several kcal/mol, are strong enough that they must be considered U-Ar bonds. We published these results in March, 2002 in *Science* (*1*). This paper garnered a great deal of attention around the world because of the fascination with the notion of direct U-noble-gas bonding. Once we discovered this effect, we were able to refine our model of it. In particular, we found that multiple noble-gas atoms could bind to CUO, a prediction that was borne out in the detection of the mixed noble-gas complexes $CUO(Ar)_{4-n}(Ng)_n$ (Ng = Kr, Xe; n = 0, 1, 2, 3, 4) (*2*, *3*). These remarkable noble-gas complexes appear to be traditional octahedral complexes, albeit complexes in which four of the coordination sites are occupied by noble-gas atoms! The predicted structures of some members of the $CUO(Ar)_{4-n}(Xe)_n$ series are shown in Figure 1.

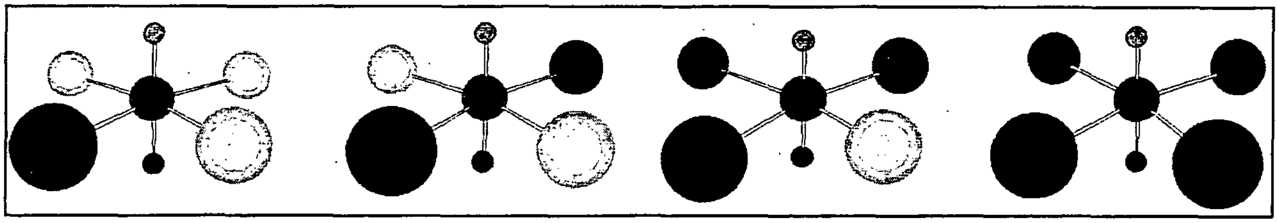

Figure 1. Calculated structures of $CUO(Ar)_3Xe$, *cis*-$CUO(Ar)_2(Xe)_2$, $CUO(Ar)(Xe)_3$, and $CUO(Xe)_4$

Our most recent work on CUO, which will continue this year, concerns a more-detailed understanding of the electronic changes in CUO upon bonding to Ar, Kr, or Xe. that allowed the U-Ng bonding to observed spectroscopically. We predicted that CUO has a low-lying excited state that corresponds to an internal charge transfer to form a U(V) triplet molecule. That excited state interacts more strongly with the noble-gas atoms than does the closed-shell ground state of isolated CUO, and with Ar, Kr, and Xe atoms, the triplet state is stabilized below the singlet. The spectroscopic signature of the triplet state is sufficiently different from that of the singlet to produce a very different vibrational spectrum. We now have theoretical and experimental evidence to indicate the number of heavy Ng atoms needed to cause the crossover of the singlet and triplet states of CUO (*4*).

We have also continued to collaborate with the Andrews group on other interesting actinide-substrate reactions. In 2002, we published an extensive study of the reactions of laser-ablated Th atoms with water molecules (*5*). These reactions led to novel products, such as the Th(II) complex HTh(OH), which results from the insertion of a Th atom into an H_2O molecule. As was the case for other small actinide complexes, our relativistic density functional calculations could be used quantitatively to explain the observed vibrational spectra and predict the structures of these new complexes.

Finally, we are continuing to use electronic structure methods to explore the speciation of actinide and actinyl ions. Some of the metal-ligand complexes have been structurally characterized by Neu and coworkers at Los Alamos, which allows for extensive testing of our methodology. A new posdoctoral associate in my group, Dr. Tianxiao Yang, has expertise in the implementation of dynamics into quantum chemical calculations. We hope these studies will ultimately provide valuable understanding about the behavior of actinide-containing ions in aqueous solutions and brines. These studies are ongoing and we are hopeful that we will have publications in this area submitted in late 2003.

Significant achievements: As noted above, the most significant achievement of this past year has been the report of the first actinide-noble gas bonds, a discovery that produced a surprising (to the PI) amount of attention. This discovery is likely responsible for some prestigious invitations that the PI has received. He will be the recipient of the Spiers Medal of the Royal Society of Chemistry at the Faraday Discussion on Quantum Inorganic Chemistry in April, 2003. He is one of only two U.S. scientists to be an invited speaker at Very Heavy Metals 2003, a conference in France in May, 2003. He also has been invited to speak at the ACS National Meeting in New York in September, 2003 in a symposium entitled Contemporary Aspects of Chemical Bonding.

Plans for future research on this project: The collaboration with Professor Andrews continues to be very fruitful. Our detailed studies of the crossover of CUO has required that we use electronic structure methods that more explicitly include electron correlation than does density functional theory. We are currently using the very highly accurate but extremely expensive coupled-cluster approach to get a better handle on the subtle energetics of this system. Also, as noted above, we look forward to making stronger contributions in the area of speciated actinide ions. We also plan to explore some of the structure and bonding aspects of some new organoactinide complexes that exhibit unusual bonding and reactivity.

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1. J. Li, B. E. Bursten, B. Liang, and L. Andrews, "Noble Gas-Actinide Compounds: Complexation of the CUO Molecule by Ar, Kr, and Xe Atoms in Noble-Gas Matrices," *Science*, **295**, 2242-2245 (2002).

2. B. Liang, L. Andrews, J. Li, and B. E. Bursten, "Noble Gas-Actinide Compounds: Evidence for the Formation of Distinct $CUO(Ar)_{4-n}(Xe)_n$ and $CUO(Ar)_{4-n}(Kr)_n$ (n = 1, 2, 3, 4) Complexes," *J. Am. Chem. Soc.*, **124**, 9016-9017 (2002).

3. L. Andrews, B. Liang, J. Li, and B. E. Bursten, "Noble Gas-Actinide Complexes of the CUO Molecule with Multiple Ar, Kr, and Xe Atoms in Noble-Gas Matrices," *J. Am. Chem. Soc.*, **125**, 3126-3139 (2003).

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Abstract P8-2

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Overall research goals. The ability to control molecular transport is pertinent to a wide variety of energy-related technologies and problems, including membrane separations, environmental remediation and uptake of biological materials, *e.g.*, pathogens, in the ambient. Central to realizing active control over molecular transport is the ability to move molecules over nanometer dimensions with high precision, selectivity, and temporal control -- a capability that would enable advances on both fundamental and technological problems. Our approach to controlling molecular transport combines actively controlled molecular assemblies with transport in confined geometries, *e.g.*, nanometer diameter channels. The broad goals of this research are to understand transport in these structures sufficiently that they can be exploited to accomplish separations and manipulations which cannot be achieved on the macroscale.

Specific objectives for 2002-2003. Our specific objectives are listed here: (1) Understand and outline the limits of performance of nanocapillary array membranes as digital nanofluidic switches; (2) Characterize how the relationship of molecular size to pore size affects transport; (3) Study the possibility of using these membranes to achieve reactive mixing with attomole-femtomole amounts of reactants; (4) Pursue the hydrogel strategy for active control of pore diameter. Significant accomplishments in these areas are described below.

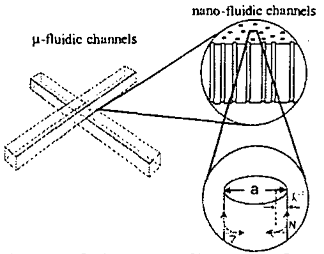

Fig. 1. Schematic diagram of the hybrid microfluidic/nanofluidic architectures based on nanocapillary array membranes, shown in cross-section in the inset.

Digital Fluid Switching. We seek to extend microfluidic devices to create hybrid three-dimensional microfluidic/nanofluidic architectures by exploiting the unique transport properties of nanocapillary array membranes. The central idea behind this set of experiments is that fluid flow is fundamentally different in physical structures of nanometer dimensions compared to larger structures, because the characteristic dimensions of the structure are approximately equal to physical scaling lengths, *e.g.*, the Debye length, $\square^{-1}$, in electrolyte solutions. This means that it is possible to effect fluid transport across nanocapillary array membranes digitally. As shown in Figure 1, nanocapillary membranes with 15- to 200-nm wide cylindrical pores can be used as interconnects to establish controllable fluidic communication between □m-scale channels operating in vertically separated planes. Crossed microfluidic channels are fabricated from polydimethylsiloxane, PDMS, in planes above and below a 5 □m thick nanoporous membrane to realize specific implementations of the generic structure shown in Fig. 1.

Size-dependent Gate Performance. Effective electrokinetic transfer from a PDMS microfluidic channel to another microfluidic channel across a nanoporous molecular gate, independent of molecular size up to 2 MDa, has been demonstrated. Molecular transport for the 15-nm pore diameter molecular gate was interrogated by a series of FITC-labeled dextrans with varying molecular size, and it was determined that for the linear dextrans, 10 kDa is the molecular size cutoff above which no discernable transport occurs.

Flow Reversal in Composite Structures. When membranes with different pore sizes are integrated with poly(dimethylsiloxane) transport devices, a remarkable effect is observed. Forward bias, which causes the Fl^{2-} containing solution to be transferred from the source channel to the receiving channel, is positive for the 15 nm and 30 nm pore diameter polycarbonate membranes, but negative for the 100 and 200 nm membranes. This behavior can be understood based on two effects – the greatly increased resistance to pressure driven flow through the smaller pores and the greater voltage drop across the pores in the 15-nm diameter case.

Reaction Profiling. The massively parallel nature of the pore structure and the typical nanometer spacing between pores in nanocapillary array membranes, led us to ask whether they could be used to mix reactive components. Scanning confocal microscopy was used to section the mixing and reaction profiles in three dimensions, demonstrating that mixing is complete at the center of the 50 □m wide intersection, which at a flow velocity of 1 mm s^{-1} indicates a 25 ms upper limit to the mixing time. This is extremely fast compared to currently available passive mixers, which require millimeter to centimeter lengths to achieve complete mixing. At the same time, the mixing ratio can be defined by the magnitude of applied bias as has been demonstrated previously. Furthermore, because the mixing is carried out in a flowing stream, imaging of the stream effectively converts position to time, so that reaction kinetics can be studied *in situ*, with sub-femtomole samples, *viz*. Fig. 2.

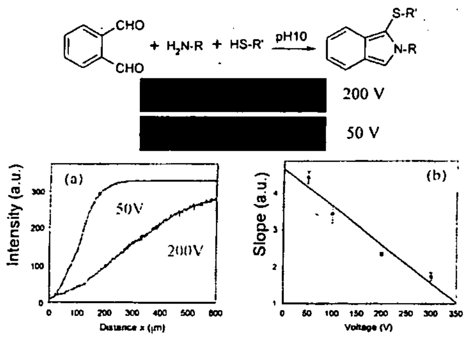

Fig. 2. Top. Schematic of the ortho-phthaldialdehyde-glycine reaction and images of the formation of fluorescent product at two different flow rates. (a) Plots of the fluorescent intensity vs. spatial position from the edge of the reaction zone at two different flow rates. (b) Slope of the linear region of the spatial intensity plot as a function of flow rate, as determined by receiving channel in-channel voltage.

Size-tunable Pores. We are working to extend the utility of these membranes by devising methods to alter the pore diameter *in situ* via grafting an electrically swellable hydrogel on the interior of the pore. Swelling properties of the thin poly-HEMA film were studied by applying a potential across the hydrogel using a two-electrode system in

0.1 M NaCl. A nanometer-scale change in polymer volume with applied potential was observed.

Plans for future research on this project. Our efforts in the coming year will extend and explore in greater detail the results presented here. In particular our goals are:

(1) Characterize the molecular weight cutoff with more resolution. Understand how the cutoff in molecular weight is related to molecular shape for these narrow pores. We want to define the molecular size transition with more resolution and to compare the results obtained with linear macromolecules to those from more globular structures. *(2) Build the hydrogels on the nanopore membranes. Characterize the response to applied potential and build the i-V characteristic for the three-terminal hydrogel-gated device.* We are ready to build electrically switchable hydrogels on the interiors of the nanopores. *(3) Characterize the reactive mixing for different analytes and for readouts without fluorescent tags.* One fluorigenic reaction uses *in vitro* selected DNA aptamer which binds Pb(II). The two strands are capped with a fluorophore and a quencher, respectively. When Pb(II) binds to the target strand, it cleaves the fluorophore-containing portion which can then be excited and emit. *(4) Build nanopores with molecular recognition elements immobilized on the interior. Characterize the binding isotherms for interior surfaces and compare to the same isotherms for binding at planar surfaces.* We will characterize single nanofluidic channels by measuring nanochannel flow and binding characteristics of individual fluorescent probes. The probes will be chosen to mate with the molecular recognition elements to be derivatized on the interior of the channels.

Publications Acknowledging DOE Support – 2002-3

T.-C. Kuo, D.M. Cannon, Jr., M.A. Shannon, J.V. Sweedler, and P.W. Bohn, "Hybrid Three-Dimensional Nanofluidic/Microfluidic Devices Using Molecular Gates," *Sens. Actuat. A*, **2003**, 102/3, 223.

P.W. Bohn, "Peptide and Protein-Based Biomolecular Assemblies: Physical and Chemical Characterization for Optimal Function," *in Biomolecular Films: Design, Function and Applications*, in press.

T.-C. Kuo, D.M. Cannon, Jr., W. Feng, M.A. Shannon, J.V. Sweedler, and P.W. Bohn, "Gateable Nanofluidic Interconnects in Multilevel Microanalytical Systems," *Analyt. Chem.*, in press.

D.M. Cannon, Jr., T.-C. Kuo, J.V. Sweedler, M.A. Shannon, and P.W. Bohn, "Nanofluidic Interconnects Produce Gated Analyte Injection for Separations and Flow Injection Analysis in Three-dimensional Microfluidic Architectures," *Analyt. Chem.*, in press.

Abstract P8-3

Density Functional Studies of Organoactinide Complexes and Actinide Oxide Materials

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Postdoctoral collaborators: Konstantin N. Kudin, Rice University

Overall research goals

The overall goal of this effort is to enhance the capabilities for calculations using density functional theory (DFT) on molecules and solids containing heavy elements and to perform applications on interesting problems in actinide chemistry.

Specific objectives for 2002-2003

In ongoing work we plan to examine the bonding and excited state properties in Cp_2UL_2 organoactinide complexes from our previous calculations to aid in the interpretation of the reactivity and absorption spectra in collaboration with our experimental colleagues J. Kiplinger and D. E. Morris (LANL). Extensions of previous work on bulk UO_2 using hybrid DFT methods to such systems as bulk PuO_2 and Pu_2O_3 and UO_2 surfaces are also planned in collaboration with Prof. Scuseria's group.

The recent recruitment of postdoctoral fellow Enrique Batista achieves an important objective since he will assume the main responsibilities for these activities. The performance of different functionals and effective core potentials in predicting thermochemistry and structures of actinide species will be assessed. We also plan to incorporate spin-orbit capabilities into DFT calculations in conjunction with relativistic effective core potentials. Initially this will be implemented for self-consistent calculations on ground electronic states as a first step towards including spin-orbit effects in excited states.

Significant achievements

During the past year we have completed a series of DFT calculations on Cp_2UL_2 complexes involving nitrogen-containing ligands (L = phenylamido, phenylimido and hydrazonato) and have examined the bonding and structures as predicted using hybrid functionals. In particular the unusual chemistry of the insertion of diazomethane into Cp_2UMe_2 to form the unusual $Cp_2U(CR_2{=}N{=}N\text{-}CH_3)_2$ species isolated by J. Kiplinger (LANL) has been investigated and contrasted with the situation in analogous Zr(IV) complexes which do not exhibit this chemistry.

Calculations on bulk UO_2 using hybrid density functional theory have been carried out, and this work represents the first such calculation on any f-element solid. Unlike previous DFT calculations that predict metallic behavior, the electronic ground state is correctly predicted to be an insulator with a gap of ~ 2 eV. Other electronic and magnetic properties are in good agreement with experimental spectroscopic observations.

Plans for future work

In future years we plan to continue investigations in actinide chemistry that involve computing reliable thermochemistries for reactions involving electronic ground states and examining reaction pathways of organometallic complexes. We also wish to be able to treat excited state properties with spin-orbit effects using variants of methods such as time-dependent DFT.

Publications

K. N. Kudin, G.E. Scuseria and R. L. Martin (2002), "Hybrid Density Functional Theory and the Insulating Gap of UO_2," *Phys. Rev. Lett.* **389**, 266402.

2. P. J. Hay (2003), "Theoretical Studies of Organometallic Complexes of Uranium Involving Nitrogen Ligands Using Density Functional Approaches," *Faraday Discussions*, **124**, in press.

Abstract P8-4

New Supramolecular-Assembly-Derived Membranes Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities

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In this new project, aimed at exploiting nanoscale porosity in separations and transport, directed-assembly techniques have been used to obtain cavity-containing supramolecular compounds. Depending on the components used, cavity diameters range from ~4 to ~22 angstroms. Advantage can be taken of the cavity structures to generate thin-film molecular materials having rationally and precisely controllable molecular sieving properties and very good molecular transport properties. Application of the materials in vapor permeation/separation studies for related aromatic or aliphatic permeants reveals up to 30-fold differences in flux, and therefore separation efficacy, for different permeant/cavity-size combinations. In collaboration with O. Yaghi, applications involving methane storage are also being explored.

We have developed polymerizable forms of these unusual cavity-containing molecules and generated thin (100 to 500 nm) polymeric membranes that show excellent size-selective transport behavior. We have also developed cavity-containing building blocks that can be used for layer-by-layer assembly of ultrathin "nanoporous" materials featuring oriented channel structures. We find that channel termini can be readily functionalized and that the functionalization engenders remarkable chemical specificity with respect to transport. Development of exceptional specificity is a current project goal.

Integrated with synthesis and applications have been: a) development of new techniques for measuring transport and other properties, and b) explanative and predictive modeling of these properties (see related poster abstract).

DOE-sponsored Papers

1. "Interfacial Polymerization of Molecular Squares: Thin Microporous Membranes Featuring Size Selective Transport", J. L. O'Donnell, M. H. Keefe, and J. T. Hupp, *Mat. Res. Soc. Symp. Proc.*, **2002**, *734*, B1.1.1 – B1.1.12.
2. "Vapor Permeation Studies of Membranes Made from Molecular Squares", K.F. Czaplewski, J.T. Hupp, and R.Q.Snurr, *J. of Membrane Sci.*, **2002**, submitted.
3. "A Perspective on Four New Porphyrin-Based Functional Materials and Devices", C.M. Drain, J.T. Hupp, K.S. Suslick, M.R. Wasielewski, and X. Chen, *J. Porph. & Phthalocyanines*, **2002**, *6*, 243-258.
4. "Ultrathin Micropatterned Porphyrin Films Assembled via Zirconium Phosphonate Chemistry", A.M. Massari, R.W. Gurney, C-H. K. Huang, M. Wightman, S.T. Nguyen, J.T. Hupp, *Polyhedron*, accepted for publication.
5. "Molecular Squares, Boxes and Cubes", P.H. Dinolfo, S-S, Sun, and J.T. Hupp, *Encyclopedia of Supramolecular Chemistry*, accepted for publication.

Abstract P8-5

Molecular Modeling and Design of Novel Nanoporous Materials for Selective Membrane Separations and Energy Storage

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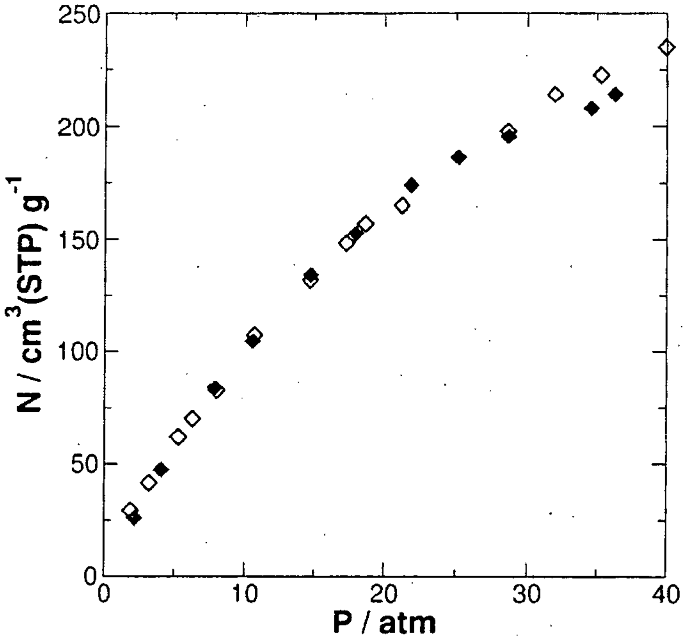
Overall research goals: The work described here uses molecular-level and multiscale modeling integrated as part of an overall project on development of novel nanoporous materials. (See additional abstract for a summary of the related experimental work.) Our development of these materials is currently focused on two applications. The first is the development of highly tailored building blocks for fabrication of membranes with very high selectivity for chemical separations. The project builds on new developments at Northwestern in nanoscale supramolecular coordination chemistry and molecular materials chemistry. We seek to exploit these developments to devise high-porosity, high-transport-rate membranes, featuring uniform pores that produce excellent separations properties due to size, shape, and chemical affinity differences in target molecules. We also seek to characterize and understand the fundamentals of selective transport in these new materials. In the second application, our target is to understand how and why novel IRMOF materials created by Yaghi and co-workers at the University of Michigan display very high uptake capacity for methane. Methane storage is important for use of natural gas as an alternative energy source. In both applications, molecular modeling can play an important role in elucidating behavior and ultimately in the design of tailored materials.

Specific objectives for 2002-2003: In the past year, our first objective was to formulate a coarse-grained model of the process used to build layer-by-layer assemblies of cavity-containing building blocks for nanoporous membranes. The second objective was to perform atomistic grand canonical Monte Carlo (GCMC) simulations of methane adsorption in IRMOF and other nanoporous materials, compare the results with experiment, and elucidate the mechanisms of methane storage.

Significant achievements: Our initial model for the layer-by-layer assembly process focused on geometric properties. A limiting case of interest is random, sequential, irreversible adsorption. Such models have been widely used for other applications (ranging from protein adsorption to parking of automobiles) and are easily formulated as simple Monte Carlo simulations. We determined the "jamming" packing densities for various shapes, including circles and squares, which are relevant to fabrication of layer-by-layer films from "molecular squares" developed by our groups. In an effort to mimic the geometric aspects of the chemistry in a simple way, the models include criteria such that new molecules will only adsorb if they overlap the necessary binding sites from the layer below. The packing densities for such random adsorption are well below those observed experimentally. This is an indication that the layers must have some ordering in the *xy* plane.

Atomistic GCMC simulations of methane adsorption were performed in a wide variety of potential adsorbents for natural gas storage: IRMOF's, molecular squares, carbon nanotubes, zeolites, and mesoporous MCM-41. Adsorption isotherms at room temperature will be presented, along with heats of adsorption, and details of molecule siting within the pores. Agreement between simulation and experimental results for the IRMOF materials is very good, using only standard potential models from the literature with no adjustment. A representative case is shown in the figure below. The simulations provide insight into the design of optimal materials for methane adsorption.



Experimental [1] (open symbols) and simulated [2] (closed symbols) adsorption isotherms for methane in IRMOF-6 at 300 K.

Plans for future research on this project: The current focus of modeling layer-by-layer growth is the formulation of a model that incorporates new experimental information that has provided new detail about the mechanisms. The model will still likely be a coarse-grained one, perhaps with some input from atomistic simulations of monolayer films. The model will seek to explain features such as characteristic changes in properties that occur beyond a certain thickness.

Given a model of a layer-by-layer material, either from our coarse-grained modeling of the growth process or from experimental evidence, we can turn to atomistic models to predict adsorption thermodynamics and diffusion rates that will control the use of such materials in membrane separations.

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2. T. D✧ren, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, manuscript in preparation.

Other publications from this project in 2002-2003:
Publications from the experimental portion of this project are listed in a separate abstract.

Abstract P8-6

Electronic Structure of Actinide Systems

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Overall research goals:

We are developing methods to compute the structure and spectra of heavy-metal systems to greater accuracy than is now possible. We also plan to compute transition moments and magnetic moments for these systems.

Actinide systems, especially actinyl ions, will be treated, including the effects of ligands on the spectra. New structures, such as polyoxo, high-valent actinide species will also be investigated.

The effect of crystalline environments on lanthanide spectra will be studied using multilayer metal-centered clusters, with high-accuracy methods used on the inner complex and simplified methods used on the outer layers.

Specific Objectives for 2002-2003:

Extensively test the relativistic quantum properties of the recent parallel version of the Columbus multireference configuration interaction programs. Extend the capabilities of the transition moment program.

Finish calculations on $U(BH_4)_4$ (spectra), UO_2 (primarily spectra), $B_4H_{10}Xe$ (binding energy, distance), and the soft X-ray spectra of UO_2^{2+}.

Significant Achievements:

UO_2 electronic spectrum. Calculation of the electronic spectrum of the UO_2 molecule to moderate accuracy has been done. Relativistic effective core potentials, double-zeta basis sets, and multireference relativistic configuration interaction were used. UO_2 has two unpaired electrons and is therefore difficult to observe. It has been studied in an inert matrix by the L. Andrews group at U. Virginia and in the gas phase (laser ablation) by the M. Heaven group at Emory U. It is linear in its ground electronic state and presumably in its excited electronic states because the two unpaired electrons are the ones being excited and they play little role in the bonding. Earlier calculations at the U. of Toulouse showed that the ground state is $(5f)^1(7s)^1$. Some time ago, the Heaven group found a dipole-allowed transition at 29,500 cm^{-1}.

Our calculations so far have used limited expansions due to restrictions in the transition moment program, which we expect to remove soon. Our results show that the excited state mentioned is due to a $7s \rightarrow 7p\sigma$ excitation and is the 31st excited state. Accordingly other dipole-allowed transitions were sought for $7s \rightarrow 7p\pi$ excitations, and they were found in the 17,000 cm^{-1} to 20,000 cm^{-1} range. A minimum of two such states are expected by angular momentum coupling, but spin-orbit mixing can spread the intensity to additional states. We have calculated lower intensities to a few other states among the 32 we studied, but these involve transitions where the major component of one of the wave functions did not contribute to the transition moment.

The states in this region are of the $(5f)^1(7l)^1$ and $(5f)^2$ types, with considerable mixing between them. The isoelectronic NpO_2^+ and PuO_2^{2+} species have only $(5f)^2$ states in this region. The 5f orbitals in $(5f)^2$ wave functions are appreciably more diffuse than 5f orbitals in $(5f)^1(7l)^1$ wave functions, due to a lower effective nuclear charge. This effect, in addition to near-degeneracies of orbitals and the spin-orbit interaction, leads to considerable multireference character in all states, requiring flexibility in the electronic structure methods used.

UO_2^{2+} X-ray spectrum. The soft (oxygen K-edge) X-ray spectra obtained by R. Denning and collaborators on $Cs_2UO_2Cl_4$ have been studied theoretically. The experimental results were obtained with the polarization vector both parallel and perpendicular to the uranyl bond axis.

The calculations are being done with a previously developed cluster model of the crystalline environment. Relativistic core potentials and double-zeta basis sets are used as for the above UO_2 work. The states being studied are well above the first ionization potential so they are really resonances and methods must be used that do not collapse to approximations to lower-energy continuum states. In this case we used multireference single-excitation relativistic configuration interaction. Correlation energy errors are small compared to the overall excitation energy. At this level of theory, localized and delocalized oxygen 1s hole descriptions give different results so were are computing both sets of values.

An important point of investigation is Denning's suggestion that some unassigned peaks correspond to excitations to U 5g orbitals.

Intensities of crystalline lanthanide transitions. We have started this study using the same methods described above. The first example is Er^{3+} transitions in a GaN host. We have obtained a new Er relativistic core potential (and spin-orbit operator) from W. Ermler and have developed a basis set for it including 5d orbitals so that 4f – 5d mixing can be described. We will build a multilayer cluster, as above, to include the crystalline environment. The four nearest N^{-3} ions will have their valence electrons treated explicitly.

Plans for future research on this project:

We plan to complete the above projects and start on some polyoxo actinide complexes, such as those originally described as actinyl(VII) species. We also plan to develop a program to compute magnetic moments for large wave functions. A start on this project is available from a previous student's work. We also hope to find time to make all of our software more usable to others because there are many more potential applications of it than we can hope to make ourselves.

Abstract P8-7

Polymers with High Permeabilities & Selectivities for Gas & Vapor Separations

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Overall research goal:

Our overall goal is to identify viable approaches to maintain the desirable intrinsic separation properties of solution-processable polyimides under aggressive separation conditions.

Specific objectives for 2002-2003:

We are studying polyimides, because of their intrinsically good transport properties. Performance achievable using two candidate techniques, (a) ionic crosslinking and (b) covalent crosslinking are being compared to *control cases* without ionic or covalent crosslinks.

Our first objective is to demonstrate the viability of both *a* & *b* as methods to stabilize the transport properties of polyimides under demanding conditions. The second objective is to determine which stabilization technique is *most attractive* for realistic conditions. To achieve these objectives, we focused on two very different model separations: (i) carbon dioxide from methane and (ii) toluene from isooctane. The first case relates to purification of natural gas, and the second case relates to aromatic-paraffin separations as alternatives to distillation.

We investigated stabilization techniques (a) & (b) for both model separations and studied different polyimide structures to show the utility of the techniques across this broad family of polymers. We reported our work at the 2002 North American Membrane Society, and will report additional work at the 2003 North American Membrane Society meeting. Also, during 2002-2003, 3 papers have appeared in print (1-3) and 3 more are in press or under review (4-6).

Significant achievements:

(i) CO_2 - CH_4 model system: For this system, covalent crosslinks appear most useful. Similar conclusion probably apply to other systems with similar sized penetrants like olefin/paraffin systems (1). Ionic crosslinks appear to be *insufficiently restrictive* to suppress swelling adequately for gas pairs with similar in sizes and shapes (2,3). Moreover, significant water activities present in natural gas would make ionic crosslinks easily disrupted.

The onset of plasticization, indicated by upturns in CO_2 permeability vs. CO_2 feed pressure, occurs at around 200 psia for typical non-crosslinked structures. On the other hand, this plasticing upturn does not occur until 700 psia for 1,4 butane diol crosslinked samples of a typical crosslinked sample we studied (1,2). This is a significant improvement in stability.

(ii) Toluene - isooctane model system: For this case, we have seen remarkably different results from those for CO_2 & CH_4. Despite repeated attempts, no covalently crosslinked samples have yet been able to withstand testing--- they shatter in the presence of the strong swelling stresses caused by exposure to the purely organic feeds. Ionic crosslinking using aluminum ions stabilized structures with lower than 33% crosslinkable content. Such samples would otherwise have literally dissolved in the feed stream. Nevertheless, these materials are still inadequate, since they still swelled extensively and showed only moderate selectivity.

It appears that a different approach to swelling control may be useful for this system. By incorporating higher amounts of carboxylic acid-containing monomers, we found that even without ionic crosslinking, hydrogen bonding attractions in such structures stabilize them against excessive swelling. Moreover, less demanding size discrimination is required compared to the case of CO_2 & CH_4, due to the larger apparent size differences between toluene vs.isooctane. Therefore, by controlling swelling via control of the *solubility parameter* of the polymer (by controlling the amount of carboxylic acid containing monomer), attractive performance occurs. Crosslinking may still be useful to optimize performance, but the benefits are less obvious than in the CO_2 - CH_4 case. More work is required to clarify this issue for this system.

Plans for future research on this project:

We are beginning to investigate an additional fascinating aspect of the polyimides used for the CO_2 - CH_4 model system. Glassy samples can eliminate excess free volume trapped during vitrification via a diffusive mechanism; however in this case, the "penetrant" comprises packets of free volume, rather than a molecule. We are especially interested in this topic, since the *mechanical properties* of even crosslinked glasses are known to show aging effects. We want to determine if aging of *transport properties* also occurs in crosslinked samples like those we have prepared for the CO_2 - CH_4 model system. This is fundamentally interesting, but it is also practically important, since the selective layers of realistic gas separation membranes are on the order of 0.1-0.5 microns.

Besides the work on the CO_2 - CH_4 model system, we will continue working to define the opportunities regarding crosslinking for the toluene-isooctane system as mentioned with regard to this highly swelling system.

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In Press and Submitted Publications from this project in 2002-2003:

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6. Wind, J. D., Sirard, S. M., Paul, D. R., Green, P. F., Johnston, K. P., Koros, W. J., "CO_2-induced Plasticization of Polyimide Membranes: Part 2: Relaxation Dynamics of Diffusion, Sorption and Swelling ", *submitted, Macromolecules.*

Relativistic all-electron calculations including the spin-orbit interaction using hybrid density functionals

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Overall research goals:

To develop accurate theoretical and computational approaches for studying the chemistry of actinides and to apply them to problems of DOE interest, especially U and Pu.

Specific objectives for 2002-2003:

To develop an all-electron density functional code able to treat the spin-orbit interaction self-consistently and analyze chemical properties of actinide-containing compounds.

Significant achievements:

Relativistic effects are known to play an important role in heavy element chemistry. They can be incorporated in quantum chemistry calculations using either pseudopotentials or all-electron methods. The former approach is faster than the latter because the number of electrons explicitly considered (and therefore the number of basis functions) is greatly reduced. All-electron methods are computationally more demanding than the pseudopotential approach, but potentially they can render more accurate results.

In our work, electron correlation effects are taken into account using density functional theory. In particular, we are interested in hybrid functionals because they are known to yield reliable results at a reasonably low computational cost. Given that we incorporate relativistic effects in the self consistent procedure, correlation and relativity are treated on the same footing.

In our all-electron approach, we include relativistic effects by means of the Douglas-Kroll[1] (DK) decoupling of the large and small components of the Dirac Hamiltonian. We use the method suggested by Hess[2] to evaluate matrix elements of operators involving the square of the linear momentum. Only the one-electron part of the Hamiltonian is transformed to include relativistic effects, while the electron-electron interaction is treated non relativistically (nuclear-only approximation). The scalar (spin-free) Hamiltonian in our calculations is decoupled to second order in the potential (DK2). The spin-orbit operator that we consider arises from the first-order spin-dependent terms in the DK transformation[3]. In the presence of the spin-orbit operator, the α- and β-blocks of the Fock matrix are coupled, and then, the Kohn-Sham (KS) orbitals (spinors) are composed by two nonvanishing spin components. The KS equations can be generalized as

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{c}^{\alpha} \\ \mathbf{c}^{\beta} \end{pmatrix} = \varepsilon \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{c}^{\alpha} \\ \mathbf{c}^{\beta} \end{pmatrix}, \qquad (1)$$

where $\mathbf{F}^{\omega\omega'}$ are the spin-blocks of the Fock matrix, $\mathbf{c}^{\omega}$ are the spinor coefficients in the atomic (real and spin-free) basis set, and $\mathbf{S}$ is the overlap matrix in that basis set. The formation of the Fock matrix for hybrid functionals involves the computation of 2 Coulomb matrices, 8 Hartree-Fock exchange matrices and 4 exchange-correlation potentials. The implementation was carried out as a stand-alone module coupled to *Gaussian Development Version*[4], using its Fock matrix formation routines.

At present we are testing the code and comparing our method with others found in the literature (Table 1). Preliminary results for the UO_2 molecule are also shown (Tables 2 and 3). In Table 1, the effect of the SO interaction in the equilibrium bond length and harmonic vibrational frequency of the TlH molecule is compared with values taken from the literature. Preliminary calculations in the UO_2 molecule show that the effect of the SO interaction has a small influence in its structure (Table 2), but it yields a substantial lowering of its HOMO-LUMO gap (Table 3).

Table 1: Equilibrium bond length, harmonic frequency and dissociation energy of the TlH molecule using different approaches.

		R_e (Å)	ω_e (cm^{-1})	D_e (eV)
HF[a] (this work)	SR DK2	1.892	1429	1.65
	SO DK2	1.875	1455	1.63
LSDA[b] (this work)	SR DK2	1.886	1379	2.76
	SO DK2	1.843	1423	1.61
B3LYP[c] (this work)	SR DK2	1.910	1358	2.16
	SO DK2	1.886	1388	1.88
HF[a]	SR ZORA[d]	1.91	1397	-
	SO ZORA[d]	1.88	1448	-
GGA[e,f]	SR DK	1.924	1323	2.72
	SO DK	1.901	1323	2.16
Experimental[g]		1.870	1391	2.06

[a] Hartree-Fock approximation.

[b] Local spin density approximation.

[c] Becke's 3 parameter hybrid functional (Ref. [5]). (SR: scalar relativistic, SO: spin-orbit included).

[d] Zero-order regular approximation, Ref. [6].

[e] Generalized gradient approximation.

[f] Ref. [7].

[g] Ref. [8].

Table 2: Equilibrium bond length, harmonic frequency of the UO_2 molecule using different approaches. A linear arrangement is assumed. See Table 1 for acronyms.

	R(UO) (Å)	$\sigma_g(^{238}U,^{16}O)$ (cm^{-1})	$\sigma_u(^{238}U,^{16}O)$ (cm^{-1})
B3LYP SR DK2	1.808	872	928
B3LYP SO DK2	1.810	867	923
PBE0[a] SR DK2	1.790	893	951
PBE0[a] SO DK2	1.794	898	956
Experimental[c]			915

[a] Perdue-Burke-Ernzerhof hybrid functional (Ref [9]).

[b] Ref. [10].

Table 3: Effect of the SO interaction on the HOMO-LUMO gap in the UO_2 molecule (in eV). See Tables 1 and 2 for acronyms.

	SR DK2	SO DK2
Hartree-Fock	17.03	16.32
LSDA	2.30	1.56
B3LYP	5.32	4.51
PBE0	6.07	5.26

Plans for future research on this project: The main plans in this project involve the following points.

- Incorporation of the 3rd order terms and 2-electron contributions in the relativistic Hamiltonian.
- Improve convergence and explore fractional occupations.
- Merge the code into the periodic boundary conditions (PBC) code.
- Excited states.

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Abstract P8-9

Investigation of Transport Mechanisms in Surface Modified Inorganic Membranes

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Research Goal

The overall objective of this project is to synthesize, characterize, and investigate the transport mechanisms in surface modified inorganic membranes for gas, vapor, and liquid separations.

Objectives for 2002-2003

Fabricate membrane by surface modification of mesoporous Vycor glass support with a fluorinated alkylsilane, heptadecafluoro-1,1,2,2-tetrahydradecyl-trichlorosilane (HDFS), $Cl_3Si(C_2H_4)C_8F_{17}$.

Compare transport characteristics of the HDFS modified membranes with those modified with octadecyl trichlorosilane (ODS) $C_{18}H_{34}SiCl_3$,

Investigate the role played by the structure of the silane layer on the transport mechanisms by synthesizing the membrane with monochlorosilane, dimethyloctadecylchlorosilane (OCS) $ClSi(CH_3)_2C_{18}H_{37}$, instead of trichlorosilane (ODS) as OCS cannot polymerize.

Accomplishments

The Cl group of the HDFS molecule reacts with the OH group on the surface of the Vycor glass (silica) support producing HCl, leaving behind the long chain hydrocarbon molecule on the surface of membrane. This reaction was utilized for the modification of Vycor glass supports with organo-silanes. Surface modification of the Vycor support was confirmed by FTIR.

As shown in Table 1, the pure gas permeances of the support decreased by 2-3 orders of magnitude after modification with HDFS. The fluoro-silane modified membrane is selective for CO_2 over hydrocarbon gases as well as lighter and smaller gases such as N_2 and He. This is a dramatic change compared to ODS modified membranes that are hydrocarbon selective. The CO_2/n-butane and CO_2/i-butane ideal separation factors for an HDFS membrane increase by factors of 23 and 44, respectively, compared to a similar Vycor support modified with ODS. The order of the pure gas permeances for the ODS modified membrane was $n\text{-}C_4H_{10}>i\text{-}C_4H_{10}>CO_2>C_2H_6>He>N_2$ and that for the HDFS membrane was $CO_2>He>C_2H_6>n\text{-}C_4H_{10}>N_2>i\text{-}C_4H_{10}$. This change in permeation characteristics of membranes with the change in the surface chemistry clearly indicates that the surface flow is one of the dominant mechanisms of transport.

The effect of temperature on pure gas permeation at constant pressure drop reveals an important characteristic of the modified membrane. Transport data for all gases show a maximum in the permeance with temperature plot, which suggests that there is more than one transport mechanism present, surface flow and activated diffusion[1]. Surface flow decreases as the temperature increases due to a decrease in surface coverage. Activated diffusion increases with temperature, which results in a maximum.

The mixed gas selectivity is higher for all the gas pairs as compared to the respective pure gas selectivity as shown in Table 1. The CO_2/C_2H_6 and $CO_2/i\text{-}C_4H_{10}$ mixed gas selectivity are approximately 178% and 36% higher then the respective pure gas selectivities. This can be explained on the basis of the competitive adsorption [2,3] in which the more interacting gas preferentially adsorbs on the surface sites blocking the access to the less interacting gas. This decreases the surface flow of the less interacting gas and hence enhances the selectivity.

We have previously hypothesized that the structure of the silane layer could be either a polymer brush or a polymerized silane layer[3]. In order to further investigate these hypotheses, we have prepared membranes modified with OCS. This monochloro alkyl silane cannot polymerize as it has only one Cl group whereas ODS can easily polymerize due to the presence of three Cl groups. So by comparing the permeance of OCS and ODS modified membranes, the structure responsible for the high reverse selective shown by these surface modified membranes may be elucidated. Both ODS and OCS membranes are selective for hydrocarbons over lighter and smaller gases such as N_2 and He. The permeances of CO_2, C_2H_6 and i-C_4H_{10} are approximately the same for both ODS and OCS modified membranes, which suggests that the interaction of these gases remains same and hence amount of surface flow is approximately the same. On the other hand, the permeances of non-condensable gases such as N_2, He and H_2 are higher by a factor of 2-5 for OCS membranes as compared to ODS membranes. As these gases have no or very little surface flow, the increase in their permeance may indicate that the OCS modified membranes have larger pores than ODS modified membranes. Investigating the effect of temperature on the transport through OCS modified membranes may also be useful.

Table 1. Summary of pure and mixed gas selectivites for HDFS modified mesoporous Vycor glass.

Selectivity	Unmodified Pure Gas	Modified Pure Gas	Modified Mixed Gas (20% CO_2)
CO_2/He	0.49	1.12	
CO_2/N_2	1.12	6.23	7.44
CO_2/CH_4		2.62	5.80
CO_2/C_2H_6		1.81	5.03
CO_2/n-C_4H_{10}	1.15	3.51	6.72
CO_2/SF_6		6.91	13.37
CO_2/*i*-C_4H_{10}		14.17	19.23

Future Work

Further characterize the surface polymer layer on the HDFS and OCS modified membranes

Perform mixed gas permeation experiments on the OCS modified membranes to study the performance of membrane and predict the dominant diffusion mechanisms.

Model the gas transport using permeance versus temperature and pressure data to obtain information about the diffusion mechanisms in the modified membranes.

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Abstract P8-10

Design of Pore Size and Functionality in Metal-Organic Frameworks for **Separation of Organics and Storage of Methane and Hydrogen**

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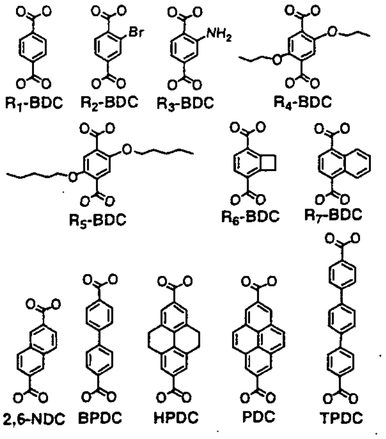
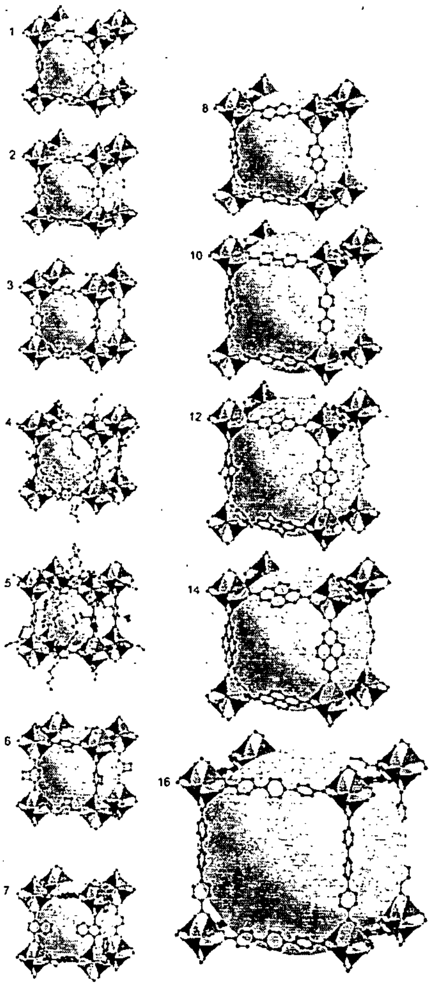
An outstanding challenge in the synthesis of crystalline solid-state materials is to alter chemical composition, functionality, and molecular dimensions systematically, that is, without changing the underlying topology. The insolubility of extended solids necessitates that their assembly be accomplished in only a single step. Thus, in order to design a target extended structure with the same precision practiced in organic synthesis, (i) the starting building blocks should have the relevant attributes necessary to assemble into the skeleton of the desired structure, (ii) the synthesis has to be adaptable to using derivatives of those building blocks to produce structures with the same skeleton but different functionalities and dimensions, and (iii) the products should be highly crystalline to facilitate their characterization by X-ray diffraction (XRD) techniques.

We have pursued the assembly of extended structures of metal-organic frameworks (MOFs) from molecular building blocks. In particular, in MOF-5, octahedral Zn-O-C clusters are linked by benzene struts to reticulate a primitive cubic structure (1, Fig. 1) and produce an exceptionally rigid and highly porous structure. Now we report the systematic design and construction of a series of frameworks having structures based on the skeleton of MOF-5, wherein the pore functionality and size have been varied without changing the original cubic topology. Several members of this series have pore sizes in the mesoporous range (>20 Å), and the lowest crystal density of any material reported to date. We also report the use of these compounds for separation of polycyclic organic molecules and for the storage of methane and hydrogen.

The design of an isoreticular metal-organic framework (IRMOF) series based on MOF-5 was initiated by determining the reaction conditions necessary to produce, in situ, the octahedral cluster with a ditopic linear carboxylate link. In this context, the original low yielding synthesis of MOF-5 was re-examined and developed into a high yielding preparation: An N,N'-diethylform-amide (DEF) solution mixture of $Zn(NO_3)_2 \cdot 4H_2O$ and the acid form of 1,4-benzenedicarboxylate (BDC) are heated (85° to 105 °C) in a closed vessel to give crystalline MOF-5, $Zn_4O(R_1\text{-BDC})_3$ (R_1 = H), hereafter termed IRMOF-1, in 90 % yield.

The simplicity of the method and the facility with which IRMOF-1 can be obtained were some of the indications that the use of other ditopic carboxylate links under closely related, if not identical, conditions would yield the same type of frameworks having diverse pore sizes and functionalities. Indeed, employing each of the links R_2-BDC, R_3-BDC, R_4-BDC, R_5-BDC, R_6-BDC, R_7-BDC, 2,6-NDC, BPDC, HPDC, PDC, and TPDC instead of BDC yielded IRMOF-2-16, including the non-interpenetrating structures of BPDC, HPDC, PDC, and TPDC. Each member of the IRMOF series has been isolated and subsequently formulated by chemical microanalysis and single-crystal X-ray diffraction studies.





All IRMOFs have the expected topology of CaB_6 adapted by the prototype IRMOF-1 (1, Fig. 1), in which an oxide-centered Zn_4O tetrahedron is edge-bridged by six carboxylates to give the octahedron-shaped secondary building unit (SBU) that reticulates into a 3-D cubic porous network. However, the IRMOFs differ in the nature of functional groups decorating the pores and in the metrics of their pore structure. In IRMOF-2 to 7, BDC links with bromide, amine, n-propoxy, n-pentoxy, cyclobutyl, and fused benzene functional groups reticulate into the desired structure wherein these groups are now pointing into the voids (2 to 7, Fig. 1). Thus we can use a wide variety of carboxylate links having a diversity of functional groups—rare aspects that heretofore remain largely absent in crystalline solid-state and porous materials research. Pore expansion is also within the scope of this chemistry, as illustrated by the structures of IRMOF-8 to 16 (Fig. 1), in which progressively longer links have been successfully employed.

Comparison of the percent free volume in crystals of IRMOF-1-16 shows that it varies in small increments (1 to 5%) from 55.8 % in IRMOF-5 to 91.1 % in IRMOF-16. Remarkably, the lowest percent free volume obtained in this series exceeds that found in some of the most open zeolites such as faujasite in which the free space is 45-50 % of the crystal volume. In fact, the fraction of free space in crystals of the expanded IRMOF series, especially those of IRMOF-8, 10, 12, 14 and 16 has only been achievable in non-crystalline porous systems such as SiO_2 xerogels and aerogels.

The calculated crystal densities (in the absence of guests) of these materials also vary in small increments (ca. 0.1) in the range 1.00 g/cm^3 for IRMOF-5 to 0.21 g/cm^3 for IRMOF-16 (Fig. 2). Moreover, the densities of IRMOF-8, 10, 12, 14, 15 and 16 are the lowest reported for any crystalline material known to date. In comparison, the density of Li metal is 0.56 g/cm^3.

The evacuated structures were found to adsorb large organic molecules present in crude oil (C12, C18, C44). The exceptionally high surface area and pore volumes observed for IRMOF-6 coupled with its appropriately designed aperture made it an ideal candidate for methane and hydrogen storage. Indeed, the methane sorption isotherm was measured in the pressure range 0 to 45 atm and room temperature, and found to have an uptake of 240 cm^3 (STP)/g (155 cm^3/cm^3) at 36 atm. The H_2 isotherm showed that up to 4.5 % wt/wt could be stored at 78 K, and up to 2 % wt/wt at room temperature and 10 bar. The presentation will discuss the use of these materials for fueling of cellular phones, laptops, and potentially automobiles.

Abstract P8-11

Analytical Applications of Single-Pore Membranes Based on Carbon Nanotubes

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Overall Research Goals

Two general and related goals have motivated our research in the area of mass transport through nanoporous membranes. The first goal is to quantitatively measure transport rate using structurally well-defined nanopores and to deduce the contribution to the overall rate from each of the four fundamental transport modes; that is, hydrodynamic, electrophoretic, electroosmotic, and diffusional. The second goal is to refine and improve the performance of Coulter counters based on single-pore membranes (Figure 1).

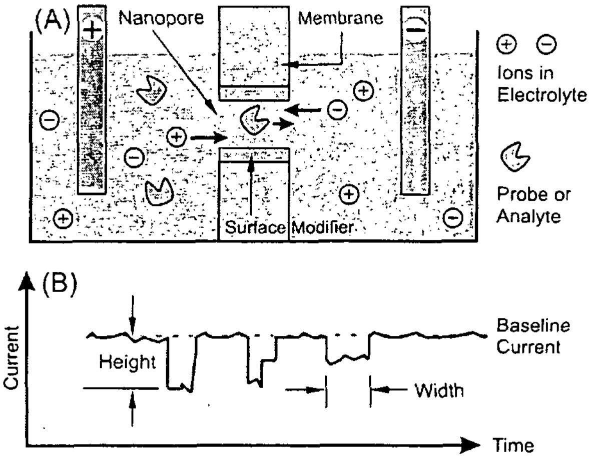

Figure 1 A Coulter counter (A) contains a single-pore membrane dividing two electrolyte solutions. Application of a voltage across the membrane results in an ion current (B). Transport of an analyte molecule through the pore causes the current to decrease momentarily. The height and the width of the current peak are related to the size and the charge of the probe.

Specific Objectives and Significant Achievements for 2002-2003

(1) Sensitivity Enhancement.[1]

We have designed novel nanoscopic counters based on carbon nanotubes to detect small particles. However, many types of experiments could not previously be carried out because the electrical signal-to-noise ratio was too high. Analogue or digital filtering could be used to remove this noise, but filtering was found to severely distort the pulse signal. We have recently discovered that membrane capacitance is closely related to the magnitude of the noise. Many other materials have been examined, but PDMS turned out to be the best (Figure 2), in terms of both its electrical properties and ease of structural fabrication.

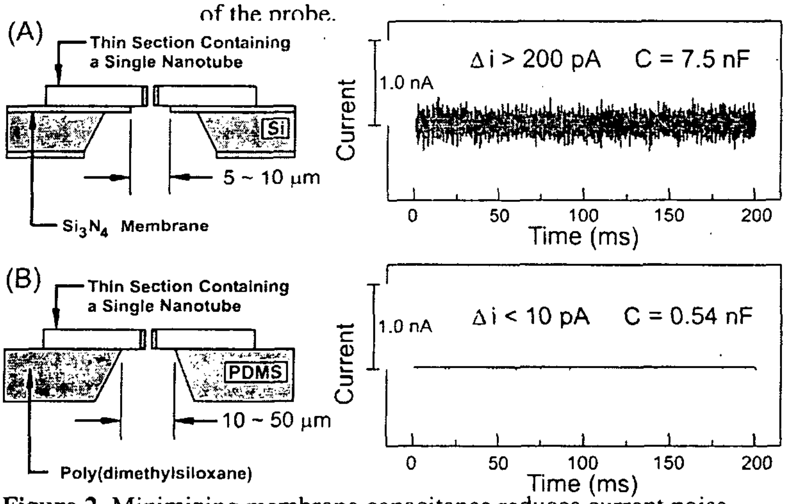

Figure 2 Minimizing membrane capacitance reduces current noise. Compared to a Si/Si_3N_4 support structure (A), a PDMS structure (B) shows a noise level more than 10 times smaller. This lowers the detection limit and allows fast current measurements (10 kHz).

(2) Simultaneous Probe Size and Charge Measurements.[2,3] A Coulter counter is normally used to size a particle from the pulse height, but under certain conditions, particle surface charge can also be calculated using the pulse width (Figure 3). This became feasible in our study for two reasons. First, the PDMS support mentioned above makes it possible to achieve a time resolution of better than 0.1 ms, which makes it possible to accurately determine transport time. Second, carbon nanotubes do not support electroosmotic flow, because the inner wall is electrically neutral. Thus, a charged probe crosses the nanotube channel exclusively via electrophoretic transport.

(3) Development of Fluorescence Microscopy for Studying Mass Transport Across Nanotubes.[2] We have been searching for optical methods for quantifying the transport rate through carbon nanotubes, and fluorescence microscopy was chosen because of its high sensitivity and potentially good time resolution. Our initial results provide a qualitative guide that will point the way to future quantitative studies. We have thus far found that if the nanotube diameter is comparable to the persistence length of DNA, then the DNA transport is limited largely by entropic trapping at the nanotube entrance. The trapping time is longer for higher molecular weight DNA.

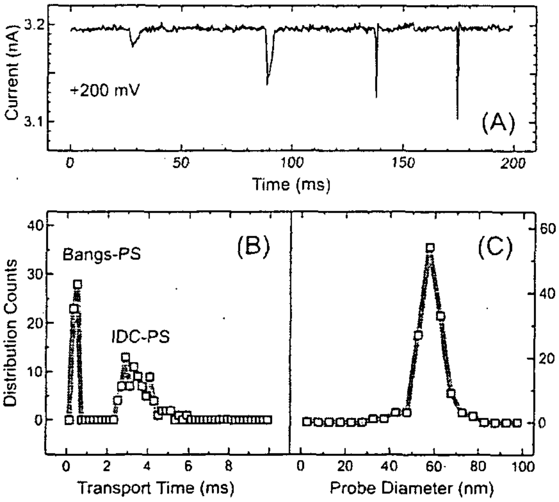

Figure 3 Distinguishing two sets of probes having similar diameters but different surface charges. Polystyrene (PS) probes from IDC have a 57 nm diameter and 120 surface COOH groups per probe, whereas the Bangs have a 60 nm diameter and 24,220 COOH groups per probe. (A) shows a representative section of the current vs. time trace. From such a trace, pulse height and width are analyzed statistically. The two sets of probes can be distinguished easily from the pulse width distribution (B), but not from the pulse height or probe diameter distribution (C).

Future Plans and Research Impact

(1) Applications of Coulter Counters for Ultrasensitive Biomolecular Detection. Soon, we will begin using our nanotube-based Coulter counter to study the transport properties of large biomolecular probes such as DNA, viruses, proteins, and antibodies. Further development of Coulter counters for bioanalysis is very important because these counters only require that an analyte has a certain geometric size, a requirement especially suited for developing general purpose detectors.

(2) Time-Resolved Fluorescence Microscopy for Mass Transport Studies. We are now trying to overcome two experimental limitations. First, in the existing detection apparatus the observation direction is along the nanotube axis, which makes it difficult to distinguish DNA entering and exiting the nanotube. This problem will be solved by adopting a horizontal nanotube geometry. Second, slow time response of our 2D-CCD prevents us from capturing real-time transport events. This problem is being solved by using single-point, high-speed photoavalanche detector.

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