**Abstract.**

Reprocessing of spent nuclear fuel with recycling of fissile isotopes is necessary to optimize energy extraction from actinide resources and to minimize waste product production. Conventional separation processing of actinides and fission products requires the use of hazardous organic solvents with relatively high disposal costs. However, novel separations processes using room temperature ionic liquids (RTIL's) either alone or in combination with supercritical fluid $CO_2$ (sc-$CO_2$) are being developed. The RTIL can be reused and the sc-$CO_2$ phase recycled, after removal of radionuclides. The overall goal of the project described here is to clarify the fundamental molecular level interactions that underlie extractions of actinides and lanthanides into RTIL'S and sc-$CO_2$. Understanding these chemical interactions will help researchers to better understand the extraction mechanisms at play in the RTIL/sc-$CO_2$ system, and to more fully optimize extraction efficiencies as well as to develop new extraction techniques. I propose to use Raman and infrared spectroscopies to study how molecular interactions between RTIL's and sc-$CO_2$ affect actinide speciation and solvation in mixtures of those solvents under differing conditions of pressure, temperature, and complexing ligand.

**Introduction.** Reprocessing of spent nuclear fuel with recycling of fissile isotopes is necessary to optimize energy extraction from actinide resources and to minimize waste product production. Conventional separation processing of actinides and fission products requires the use of hazardous organic solvents with relatively high disposal costs. The United States will need to consider developing new energy sources in the next several years, and nuclear energy is likely to grow in importance. However, gaining public acceptance of nuclear technology will require the development of environmentally sustainable methods for nuclear fuel recycling and nuclear waste management. Emerging novel separations processes can safely and effectively separate the useful components of discharged nuclear fuel from the wastes, while dramatically reducing the volume and toxicity of the wastes. In one such process, radionuclides from aqueous wastes or solid waste forms are transferred to a room temperature ionic liquid (RTIL) phase, from which they are extracted into a supercritical $CO_2$ (sc-$CO_2$) phase. The RTIL phase can be reused and the sc-$CO_2$ phase can also be recycled, after removal of radionuclides. The solvent properties of the sc-$CO_2$ phase can be changed, or tuned, by changing pressure and temperature; thus, it is potentially possible to design selective extractions of lanthanides and actinides from the RTIL phase to the sc-$CO_2$ phase.[1] The chemistry of the actinide elements is extremely rich, and much of that chemistry as yet remains uncharted. One gap in our fundamental understanding of actinide chemistry relates to the largely unexplored chemical behavior of actinides in RTIL's and sc-$CO_2$. The overall goal of this project is to begin to fill that gap by examining the solvation and coordination chemistry of actinides and other f-elements in RTIL's and sc-$CO_2$.

**Objectives and Methods.** While RTIL's and sc-$CO_2$ are promising solvents, information on the solvation and coordination chemistry of actinides and other f-elements in these liquids is lacking, and information obtained in standard solvent systems cannot with any certainty be applied to these alternative solvents. The chemical behavior of f-elements in RTIL's and sc-$CO_2$ has only begun to be elucidated.[2-7] An in-depth understanding of actinide solvation and coordination chemistry is essential for a more full understanding of the extraction mechanisms at play in the RTIL/sc-$CO_2$ system. It is also important for the optimization of extraction efficiencies, and the development of new extraction techniques. I propose to use Raman and infrared spectroscopies to study actinide solvation and coordination chemistry in RTIL's and sc-$CO_2$, as well as to determine how molecular interactions between RTIL's and sc-$CO_2$ affect actinide speciation and solvation in mixtures of those solvents under differing conditions of pressure, temperature, and complexing ligand. My specific objectives for the one year time-frame are as follows:

**1** Investigate the solvation chemistry and speciation of uranyl(VI) in sc-$CO_2$, RTIL's, and sc-$CO_2$/RTIL mixtures under differing conditions of pressure, temperature, and complexing ligand. Determine how changes in pressure and temperature affect the solvation chemistry and speciation of uranyl(VI) species in RTIL/sc-$CO_2$ mixtures. Ligands may include those important in nuclear waste processing: tri-*n*-butylphosphate (TBP), tri-n-butylphosphine oxide (TBPO), trioctylphosphine oxide (TOPO), and triphenylphosphine oxide (TPPO). These compounds are chosen because they are soluble in sc-$CO_2$ and show high extraction efficiencies for uranyl(VI).[8]

**2** Investigate the specific molecular-level interactions between sc-$CO_2$ and RTIL's, sc-$CO_2$ and uranyl(VI) species and between RTIL's and uranyl(VI) species under differing conditions of pressure and temperature. Determine the effect of pressure and temperature on these interactions.

I propose to use Raman spectroscopy and infrared spectroscopy for this research because vibrational modes are very sensitive indicators of changes in molecular environment, and can be used to elucidate the equilibrium distribution of actinides in various solvents. For example, I have previously used the Raman-active $\nu_s(UO_2)$ (symmetric stretching) mode to study uranyl(VI) complexation with citric acid in aqueous solutions,[9] and the infrared-active $\nu_{as}(UO_2)$ (asymmetric stretching) mode to study uranyl(VI) complexation with nitrate in an RTIL.[10] Raman and infrared spectroscopies can also be used to track changes in ligand vibrational modes upon complexation, and to examine the chemical interactions between sc-$CO_2$ and RTIL's under varying conditions of pressure, temperature, and solute (uranyl-ligand complex, for example). Raman and infrared spectroscopies can thus provide molecularly-specific information as to how changing solvent conditions affect the solvation chemistry and speciation of actinides in sc-$CO_2$, RTIL's, and sc-$CO_2$/RTIL mixtures. The information I will obtain will enable me to understand the chemical basis underlying optimal and suboptimal extraction conditions for actinide metals in the RTIL/sc-$CO_2$ system.

Raman spectra of actinide species in RTIL's will be acquired using standard Raman cells suitable for work at atmospheric pressure and a Renishaw Ramascope Raman microscope with a 785 nm laser. Infrared spectra at atmospheric pressure will be acquired using an attenuated total reflectance (ATR) accessory and an FTIR spectrometer. Measurements in sc-$CO_2$ and sc-$CO_2$/BMIM-$Tf_2N$ mixtures will be acquired using a high pressure supercritical fluid system, which will include a high-pressure flow-through Raman cell and a supercritical fluids pump and controller. The Renishaw Ramascope system, an ATR accessory for work at atmospheric pressure, a FTIR spectrometer, and a supercritical fluids pump and controller are available in my research laboratory. A high-pressure flow-through Raman cell will be constructed.

**Potential Impact and Expected Outcomes.** Nuclear chemistry has played a vastly important role in United States history since the end of World War II, and the United States has long been recognized as a leader in this area of research. In recent years, however, the numbers of American universities offering a specialization in nuclear and/or radiochemistry has decreased, along with the numbers of active faculty in that field.[11] However, there is still a great need for fundamental research in these areas because of the necessity of resolving issues related to nuclear waste disposal, nuclear weapons management, nuclear non proliferation, and the environmental remediation of contaminated sites. The knowledge gained in this study relates to nuclear waste disposal issues and will be disseminated through papers, meeting presentations, and other scholarly output. This information will be of interest to the nuclear chemistry community, and may be applied in a practical fashion to the reprocessing of nuclear fuels and wastes. In addition, the information gained in this study will be used to provide impetus for future proposals I intend to submit to the Department of Energy and the National Science Foundation.

One of the most important broad impacts of this research involves the training of the next generation of U. S. nuclear chemists. One undergraduate student will be hired to assist with my research on this project. I am strongly committed to recruiting, mentoring, and training students with an interest in nuclear chemistry, as they are vital to the future of U.S. nuclear chemistry.

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