

Complexation of Actinides in Solution: Thermodynamic Measurements and Structural Characterization

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Abstract

This paper presents a brief introduction of the studies of actinide complexation in solution at Lawrence Berkeley National Laboratory. An integrated approach of thermodynamic measurements and structural characterization is taken to obtain fundamental understanding of actinide complexation in solution that is of importance in predicting the behavior of actinides in separation processes and environmental transport.

Introduction

Fundamental understanding of the complexation of actinides in solution is of great importance in the development of efficient separation processes as well as the environmental management of nuclear wastes. My research program at Lawrence Berkeley National Laboratory focuses on the study of actinide complexation with organic and inorganic ligands that could have impact on the behavior of actinides in spent nuclear reprocessing or environmental transport. This program has two major thrust areas: 1) thermodynamics of actinide complexation (including hydrolysis) at elevated temperatures; 2) thermodynamics and structure of actinide complexes with ligands of interest in actinide separations and environmental transport. An integrated approach of thermodynamic measurements and structural characterization is taken in the research. The results from this research program, while supporting U.S. Department of Energy's mission of safe management of nuclear wastes and development of advanced nuclear fuel cycles, provide insight into the fundamental aspects of actinide coordination in solution.

Thrust Area I: Complexation (including hydrolysis) of actinides in solution at elevated temperatures

There has been significant interest in the studies of the complexation of actinides with organic and inorganic materials in solution at elevated temperatures due to the demands for scientific information to aid the safe management of nuclear wastes. The temperature of nuclear wastes in the storage tanks and the vicinity of the waste repository is known or estimated to be significantly above the ambient temperature. For example, the temperature in the storage tanks is up to 90°C and the temperature in the nuclear waste repository could be close to 100°C thousands of years after the closure of the repository. Failure of the engineering barriers of the waste form could result in the contact of nuclear wastes with groundwater and possible

migration of actinides in the environment. Prediction of the chemical behavior of actinides in waste processing and in the repository requires the thermodynamic data on the complexation of actinides at elevated temperatures. At present, the majority of the thermodynamic data on actinide complexation are obtained at or near 25°C. The lack of data at elevated temperatures makes it difficult to predict the behavior of actinides in the waste processing and disposal where elevated temperatures are expected.

While providing data to support the safe management of nuclear wastes, studies of the complexation of actinides at elevated temperatures could improve the fundamental understanding of the coordination chemistry of actinides as well. For example, the change in temperature perturbs the structure of solvent in the bulk and in the vicinity of the ions, alters its dielectric property and thus affects the energetics of the complexation. Therefore, the trends in thermodynamic parameters over a wide range of temperature could provide insight into the nature of the actinide complex and the solvent effect.

We have recently studied the complexation of actinides with a series of carboxylic acids and inorganic ligands in solution in a temperature range up to 85°C [1-4]. Variable-temperature potentiometry, calorimetry and spectrophotometry are used to determine the equilibrium constants and the enthalpy of complexation. Results indicate that the complexation of actinides with carboxylates and the hydrolysis of actinides are enhanced at elevated temperatures (Fig.1). The enhancement is attributed to the changes of the properties and structure of water caused by the change in temperature. The hydrolysis of actinides becomes stronger at elevated temperatures mainly due to the increase of the ionization of water. The complexation of actinides with carboxylate ligands is entropy-driven and becomes stronger when the temperature is elevated due to the increasingly larger entropy of complexation at higher temperatures. Combined with the structural information on the actinide complexes obtained by spectroscopic techniques, the thermodynamic data provide insight into the fundamental nature of actinide

complexes and the energetics of complexation, and help to predict the speciation of actinides in solution at elevated temperatures.

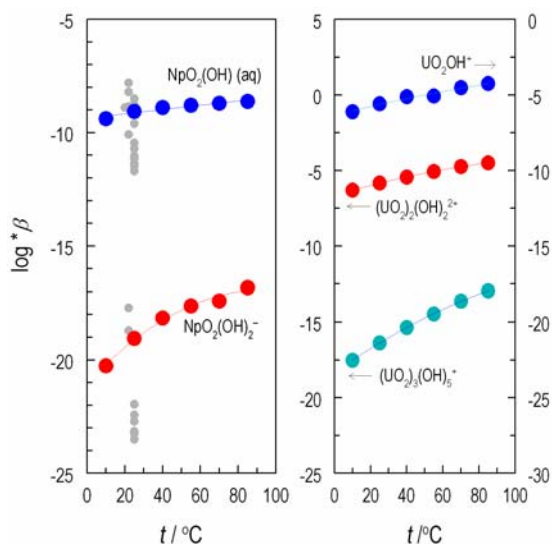


Fig 1 Hydrolysis of U(VI) and Np(V) at variable temperatures [2,3].

Thrust Area II: Complexation of actinides with ligands that are of importance in actinide separations

There has been significant interest in recent years in the studies of alkyl-substituted amides as extractants for actinide separation because the products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes than those of organophosphorus compounds traditionally used in actinide separations. Stripping of actinides from the amide-containing organic solvents is relatively easy. In addition, the amide ligands are completely incinerable so that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.

One group of alkyl-substituted oxa-diamides have been shown to be promising in the separation of actinides from nuclear wastes. For example, tetraoctyl-3-oxa-glutaramide and tetraisobutyl-oxa-glutaramide form actinide complexes that can be effectively extracted from nitric acid solutions. To understand the thermodynamic principles governing the complexation of actinides with oxa-diamides, we have studied the complexation of lanthanides and actinides (Nd(III), Th(IV), Np(V) and U(VI)) with dimethyl-3-oxa-glutaramic acid (DMOGA) and tetramethyl-3-oxa-glutaramide (TMOGA) in aqueous solutions, in comparison with oxydiacetic acid (ODA). Thermodynamic

parameters of complexation (stability constants, enthalpy and entropy of complexation) were measured by potentiometry, spectrophotometry and calorimetry. Spectroscopic techniques and X-ray crystallography were used to identify the structures of complexes. The results help to develop a structure-property relationship that could guide the design of new ligands to improve the binding strength and the extraction efficiency. The crystal structure of a highly symmetric Np(V) diamide complex was identified by using the beam line for small-molecule X-ray crystallography at the Advanced Light Source (Fig.2). The structure of the complex helps to interpret the absence of *f-f* transitions in the optical absorption spectra of the Np(V)/diamide complex [5].

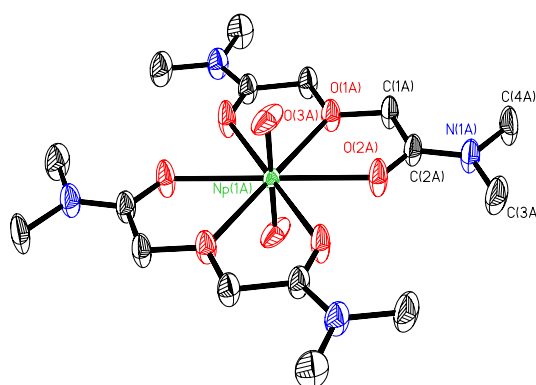


Fig 2 ORTEP drawing (30% probability ellipsoids) of $[\text{NpO}_2(\text{L}^{\text{II}})_2]^+$ [5].

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