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Actinide Thermodynamics at Elevated Temperatures

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ACTINIDE THERMODYNAMICS AT ELEVATED TEMPERATURES

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RESEARCH OBJECTIVES

The postclosure chemical environment in the proposed Yucca Mountain repository is expected to experience elevated temperatures. Predicting potential migration of actinides would be more robust if sufficient reliable thermodynamic data on hydrolysis and complexation are available for these temperatures. Data are scarce and scattered for 25°C, and nonexistent for elevated temperatures. Current modeling of actinide migration makes conservative assumptions to compensate for this lack of data, particularly at elevated temperatures.

This collaborative project between LBNL and PNNL collects thermodynamic data at elevated temperatures on actinide complexes with inorganic ligands that may be present in Yucca Mountain. The ligands include hydroxide, fluoride, sulfate, phosphate and carbonate. Thermodynamic parameters of complexation, including stability constants, enthalpy, entropy and heat capacity of complexation, are measured with a variety of techniques including solvent extraction, potentiometry, spectrophotometry and calorimetry.

APPROACH

Acid-base potentiometry measures electromotive force (*emf*) as a function of the concentration of hydrogen ion that in turn depends on the reactions in solution including ligand protonation and metal complexation. Thus the measured *emf* can be used to calculate the stability constants of actinide complexes. Solvent extraction uses the change of distribution coefficients with the ligand concentration to determine metal complexation stability constants. With spectrophotometric methods, the oxidation states and nature of actinide species are identified by characteristic absorption bands (e.g., Np(V) at 980 nm and Pu(VI) at 830 nm). From the change of absorbance as a function of concentrations of reagents, the stability constants of actinide complexes are determined. Nuclear magnetic resonance (NMR) spectroscopy measures chemical shifts in species of nuclei present according to fractional populations. Since the magnitude of chemical shifts depends on the values of the equilibrium constant, the chemical shift becomes a function determined analogous to the potentiometric case.

Titration calorimetry directly measures reaction heat released (or absorbed) when a solution is titrated with a titrant. Since the reaction heat in a complexation titration is a function of the concentrations of reagents, the stability constant(s) of complex(es) and the enthalpy of complexation, the latter can be calculated from calorimetric titrations.

ACCOMPLISHMENTS

Complexation of Pu(IV) and Pu(VI) at elevated temperatures. Thermodynamic studies of actinide complexation at elevated temperatures were extended from uranium and neptunium to plutonium, another important transuranic element of great concern in environmental transport. Complexation of Pu(IV) with F$^-$ was studied at $25 - 55$^{o}C by solvent extraction (Fig.1). The equilibrium constants of the reactions, $Pu^{4+} + iHF = PuF_i^{(4-i)+} + iH^+$ where $i = 1$ and 2, were found to decrease with increasing temperature.

[Insert Figure 1 here]

Complexation of Pu(VI) with F$^-$ and SO$_4^{2-}$ was studied at 25°C by spectrophotometry using the characteristic absorption band of Pu(VI) at 830 nm (Fig.2). Calculations of stability constants are in progress.

[Insert Figure 2 here]

Spectrophotometric measurements on Np(V) and U(VI) at elevated temperatures. Spectrophotometric titrations were performed to measure the stability constants of $U(VI)/F^-$, $U(VI)/SO_4^{2-}$, $Np(V)/F^-$ and $Np(V)/SO_4^{2-}$ complexes at 25 - 70°C. It was found that all these complexes become stronger at higher temperatures.

[Insert Figure 3 here]

Microcalorimetric measurements on Np(V) and Pu(VI). Calorimetric titrations of $Np(V)/F^-$ and $Np(V)/SO_4^{2-}$ complexes were completed and data processing with new stability constants obtained by spectrophotometry is in progress. A representative calorimetric titration is shown in Fig. 4. Calorimetric titrations of Pu(VI) systems have been started.
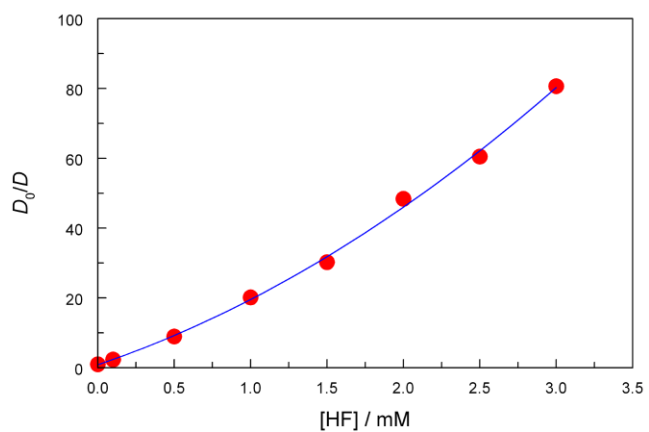
[Insert Figure 4 here]

Fig. 1 Solvent extraction of Pu(IV) in the presence of HF: Plot of D_0/D vs. [HF], solid symbol − experimental, curve - calculated. Aqueous phase – Pu(IV) in 2.0 M $HClO_4$ + HF; organic phase – 0.05 M TTA in toluene; t = 55°C.
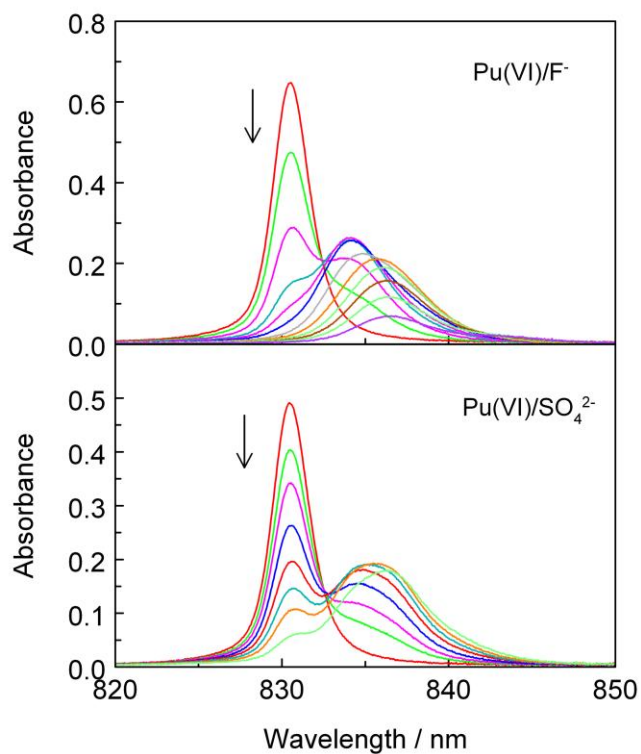
Fig. 2 Spectrophotometric titration of Pu(VI) complexation with fluoride and sulfate (I = 1.0 M NaClO$_4$, t = 25°C, optical path = 1.00 cm). Top - Pu(VI)/fluoride: V^0 = 2.50 mL, C_{Pu}^{0} = 1.18 $\times$ 10^{-3} M, C_{H}^{0} = 1.51 $\times$ 10^{-3} M; titrant: 1.00 M NaF, 3.29 mL added. Bottom – Pu(VI)/sulfate: V^0 = 2.50 mL, C_{Pu}^{0} = 8.93 $\times$ 10^{-4} M, C_{H}^{0} = 1.14 $\times$ 10^{-3} M; titrant: 0.50 M Na$_2$SO$_4$, 1.50 mL added.
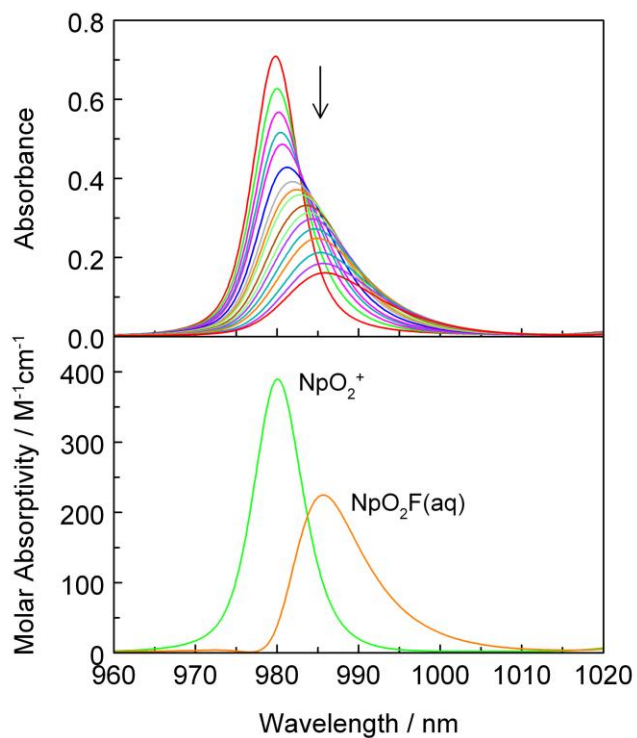
Fig. 3 Spectrophotometric titration of Np(V) fluoride complexation (I = 1.0 M NaClO$_4$, t = 25°C, optical path = 1.00 cm). Top − 17 spectra, V^0 = 2.50 mL, C_{Np}^0 = 1.82 × 10^{-3} M, C_H^0 = 1.0 × 10^{-6} M; titrant: 1.00 M NaF, a total of 2.40 mL added in 16 additions. Bottom − calculated molar absorptivities of Np(V) species.
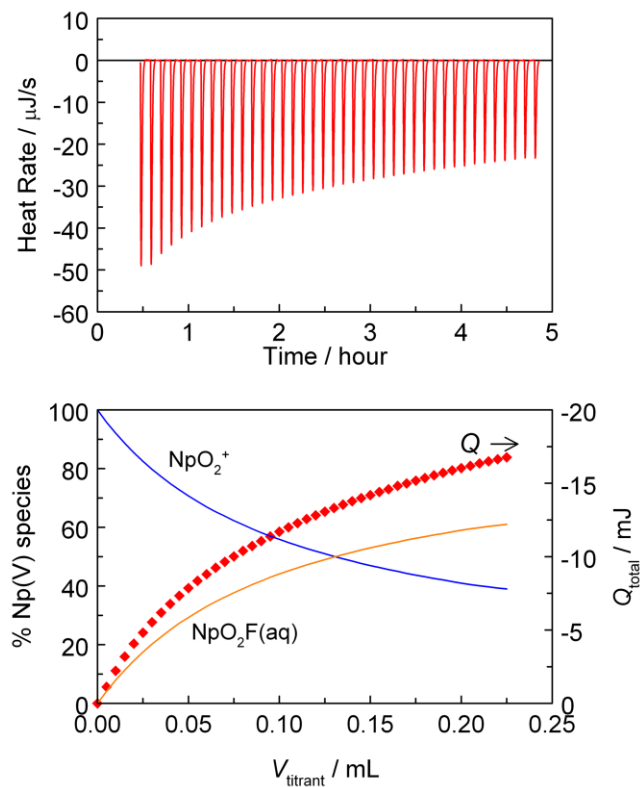
Fig. 4 Calorimetric titration of Np(V) fluoride complexation (I = 1.0 M NaClO$_4$, t = 25°C). V^0 = 0.900 mL, C$_{Np}^0$ = 1.78 $\times$ 10^{-3} M, C_H^0 = 3.0 $\times$ 10^{-7} M; titrant: 1.0 M NaF, 5 microL/addition.