Chemical Thermodynamics of Actinide Coordination in Solution at Variable Temperatures

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The temperature in the nuclear waste storage tanks and in the vicinity of high-level nuclear wastes in the repository could be significantly higher than 25 ^{o}C due to the decay energy of radioactive materials. Thus, reliable models for predicting the chemical behavior of actinides in the waste processing and in the "near-field" environment must properly take into consideration the temperature effect on the coordination of actinides with ligands that may be present. Currently, very few data are available on the coordination of actinides at elevated temperatures. The approximation methods, including the "constant enthalpy" approach, the "constant heat capacity" approach, the DQUANT equation and the revised HFK equation, have not been extensively tested because of the lack of experimental data. To extend the thermodynamic database to include the effect of temperature on the coordination of actinides, a research program has been started at Lawrence Berkeley National Laboratory to investigate the coordination of actinides in solution at variable temperatures.

Coordination of actinides (III, IV, V, VI) by carboxylate ligands and hydroxide is studied at 10 – 85 ^{o}C. Equilibrium constants and the enthalpy of reaction at variable temperatures are determined by potentiometry and calorimetry. From these data, the entropy and the heat capacity of reaction in the temperature range are calculated. Applicable spectroscopic techniques, including optical absorption, fluorescence and X-ray absorption, are used to provide insight into the nature and energetics of the coordination.

The complexation of actinides with carboxylate ligands ($M + nL = ML_n$) usually becomes stronger when the temperature is elevated, due to the increasingly larger entropy of complexation at higher temperatures. The hydrolysis of actinides ($mM + nH_2O = M_m(OH)_n + nH$) is also enhanced at elevated temperatures, partly due to the increase of acidity of water with increasing temperatures. These experimental data allow extensive testing and comparison of the commonly used approximation approaches to account for the effect of temperature on the coordination of actinides.