Measurement of the Enthalpies of Complexation of Thorium with Multiple Fluoride Ligands

P. M. Grant,1 W. F. Kinard,2 and P. A. Baisden1
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Titration calorimetry has been utilized to study the aqueous solution chemistry of the Th4+ + F− system. Enthalpies of the first three complexation reactions have been measured at an ionic strength of 0.5M at 25°C, and corresponding entropy values have been calculated. Results for the first complex are in good agreement with an established electrostatic model of metal-fluoride bonding.

KEY WORDS: Thorium; fluoride; complexation; enthalpy; calorimetry; ionic bonding.

1. INTRODUCTION

This paper reports the results of a study of the complexation of Th4+ with the fluoride anion through the utilization of a very sensitive solution calorimeter.1) Thorium is of interest in our laboratory primarily by virtue of its membership in the actinide series. It can serve as a useful analog of Pu(IV) chemistry,2) while the lower radioactivity and toxicity of Th facilitate its use in an experimental program. Fluoride is of intrinsic interest in coordination chemistry3,4) and can also be an important component in applied and environmental studies. For example, F− is present at ppm concentrations in groundwater from tuff formations in the Yucca Mountain vicinity of the Nevada Test Site.5) At these levels, it must be considered as a potentially significant factor in the migration of high-level radioactive waste from a geologic repository over long time periods. The calorimetric investigation of the Th4+ + F− system was a natural extension of recent work in our laboratory on the thermodynamics of lanthanide-fluoride complexation.6,7)

Formation enthalpies for the second and third complexes of Th4+
with F\(^-\) at a moderate ionic strength \(\mu\) have not previously been published. Baumann\(^{(8)}\) does report infinite-dilution values calculated from van't Hoff analyses of stability-constant measurements, however, and Ahrland\(^{(9)}\) lists unpublished, work-in-progress data at \(\mu = 4M\). Data do exist in the literature for \(\Delta H_{101}\) of ThF\(^{3+}\) at \(\mu = 1.0M\ (\text{HClO}_4)\) and 25°C.\(^{3}\) Choppin and Unrein\(^{(10)}\) measured values of 1.1, 2.3, and 3.0 kJ-mol\(^{-1}\) by means of solvent extraction, potentiometry, and calorimetry, respectively. Martell and Smith’s most recent evaluation inexplicably gives a value of 15 kJ-mol\(^{-1}\) for this enthalpy,\(^{(11)}\) but their number may well be a typographical error.

Theoretical considerations can provide some guidance as to what to expect thermodynamically from the formation of the first Th-F complex. A previously-established correlation\(^{(3)}\) between Coulomb potential energy and \(\Delta S_{101}\) for metal-fluoride complexes at \(\mu = 1M\) can be used to predict the formation entropy of ThF\(^{3+}\) from the ionic radius of Th\(^{4+}\). These systematics in conjunction with \(\Delta G_{101}\) lead to a prediction of 1.4 kJ-mol\(^{-1}\) for \(\Delta H_{101}\).

2. EXPERIMENTAL

A 0.02M Th\(^{4+}\) working solution was prepared from 99.99%-pure thorium nitrate (Spex Industries), acidified to pH 1.1 with HClO\(_4\), and adjusted to \(\mu = 0.5M\) with NaClO\(_4\). The titrant was 0.1M NaF at pH 6.4 and \(\mu = 0.5M\) (NaClO\(_4\)). Details of reagent purification, assay, etc., have been presented elsewhere,\(^{(6,7)}\) and all materials were of analytical reagent-grade quality or better.

The description and operation of the adiabatic titration calorimeter utilized for these experiments has been previously published.\(^{(1)}\) The initial volume of the titrated Th\(^{4+}\) solution was 50 ml, while titrant was typically added in aliquots of 0.50 ml. The entire range of metal-fluoride speciation up to the point of ThF\(_4\) precipitation was sampled in this study, and precipitation occurred at an average ligand number \(\bar{n} > \approx 1.7\) in this system.

In addition to Th\(^{4+}\) + F\(^-\) titrations, experiments were performed in which fluoride was titrated into \(\mu = 0.5M\), pH = 1.4 HClO\(_4\) to measure \(\Delta H_{011}\) at this ionic strength. Heat-of-dilution or blank runs were accomplished by titrating 0.5M NaClO\(_4\) solution with fluoride.

\(^{3}\)The indices "101" refer to the number of atoms of metal, hydrogen, and ligand, respectively, in the complex. Thus, "101" indicates the reaction M + F \(\rightleftharpoons\) MF, "011" indicates H + F \(\rightleftharpoons\) HF, etc.