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Solution Thermodynamics of Europium–Fluoride Complexation

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Abstract

The enthalpy of formation of EuF^{2+} in solution has been redetermined by titration calorimetry. Experiments at a constant ionic strength of $\mu = 1.0$ M ($NaClO_4$), but at a variety of fluoride titrant concentrations, gave $\Delta H_{101} = (9.61 \pm 0.03)$ kJ/mol at 25 °C. This value is considerably lower than that previously reported in the literature. The corresponding entropy, however, is now consistent with an electrostatic model which has been shown to describe the behavior of a wide variety of metal–fluoride complexes.

Introduction

Initial experimentation with a newly-developed titration calorimeter [1] focused on the enthalpies of formation of the monofluoride rare-earth complexes. Although a thorough study of these systems had been performed at 25 °C and an ionic strength of 1.0 M [2], we attempted to verify the original work and duplicate those results as a check of our calorimeter system prior to studying more complicated three-component systems.

For all monofluoro-lanthanide complexes investigated, our results for the enthalpy of complexation (ΔH_{101}) were consistently factors of 3–4 lower than the existing literature values. To investigate this discrepancy in detail, we chose a representative lanthanide (Eu) and performed a number of experiments at different fluoride titrant concentrations. This paper presents the results of that investigation.

Experimental

Calorimeter

Our high-sensitivity titration calorimeter [1] operates in an adiabatic mode and is similar in principle to the instrument already described by Caceci and Choppin [3]. All functions of the titration system are performed under software control using an IBM personal computer. Peltier cooling offsets the heat of stirring such that the allowed temperature drift is < 0.75 μ °C/s. Changes in the heat capacity of the system are taken into account by performing electrical calibrations before and after each titrant addition. Calibration heats and heats of reaction are measured by means of a thermistor immersed in the experimental solution. The thermistor is coupled to a Wheatstone bridge which converts the change in resistance of the thermistor with temperature to a voltage signal. Changes in voltage are detected by a nanovolt null circuit, digitized, and read by the computer via an IEEE-488 bus. Precise volumes of titrant are dispensed to the reaction cup by means of a Radiometer ABU80 Autoburette, and all reactants are equilibrated at 25.0000 ± 0.00025 °C in a Tronac 95-liter water bath.

The accuracy of our calorimeter system was determined by measuring the heat of protonation (ΔH_p) of TRIS [tris(hydroxymethyl)-aminomethane] as a primary calibration standard [4]. From 80 replicate analyses, our measured result for ΔH_p was (-47.44 ± 0.50) kJ/mol. This value is in excellent agreement with the recommended value of (-47.44 ± 0.05) kJ/mol derived from Grenthe's work [5] and demonstrates the satisfactory performance of our calorimeter system.

Materials and Methods

The Eu stock solution was prepared by the dissolution of 99.999% pure Eu_2O_3 (AESAR Reaction Grade) in $HClO_4$. Following filtration and adjustment to pH ~ 2.5 with $HClO_4$, the solution was assayed colorimetrically for Eu by complexometric titration using EDTA with xylenol orange as the metal indicator. The calorimeter working solutions ([Eu] $\sim$ 0.035 M) were made from the stock solution by dilution and adjusted to $\mu = 1.00$ M with $NaClO_4$. The hydrogen ion concentration was determined using a combination glass electrode calibrated with solutions of known $[H^+]$ in 1.0 M $NaClO_4$ media. For a calorimeter run, 50.0 ml of the Eu working solution was used.

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Fluoride titrants consisted of 0.025 M, 0.05 M, and 0.1 M NaF solutions at pH ~ 6, adjusted to μ = 1.00 M with $NaClO_4$. These solutions were prepared determinantly from reagent NaF that had been purified by the method of Lingane [6]. Class A volumetric apparatus and analytical reagent-grade quality (or better) materials were used throughout this work.

Each calorimeter run required a total of 15–20 successive additions of constant 0.25- or 0.50-ml aliquots of titrant into the reaction cup containing the Eu solution. The data reported are the results of replicate experiments at each titrant concentration.

Computations and Data Analysis

The output from each calorimeter run consisted of the change in temperature (ΔT) effected by each addition of titrant [1], as well as the system heat–capacity data (joules/ΔT) as a function of solution volume. An instrumentally-weighted, linear-regression fit to the calibration data (heat capacity *versus* titrant addition) was computed by means of a BASIC program analogous to Bevington's CURFIT routine [7]. This calibration line was then used to convert the measured ΔT to joules of energy for each addition of titrant.

The heat generated or absorbed by an aliquot of titrant is partitioned among three general pathways: $Eu^{3+} + F^-$ complexation reaction(s); the formation or destruction of HF; and the heat-of-dilution of titrant. The heat-of-dilution was measured in separate, blank calorimeter runs and was found to be a second-order correction (~0.001 J) to the overall experimental heat (~0.1 J).

Dividing the total heat between reactions of the fluoride ion with metal (EuF_x) and with hydrogen ions (HF) requires detailed knowledge of the solution speciation at each point of the titration. We calculated complete system speciation with our program FNEWT. With inputs of initial solution compositions, volumes, and acid and stability constants of all reacting species, FNEWT uses the Newton-Raphson method [8] with an appropriate convergence criterion to iteratively compute the speciation at each point in the titration. The relevant equilibria and constants input to FNEWT were:

$$Eu^{3+} + F^- \rightleftharpoons EuF^{2+} \quad K_1 = 1860, \log \beta_{101} = 3.27$$

$$EuF^{2+} + F^- \rightleftharpoons EuF_2^+ \quad K_2 = 423, \log \beta_{102} = 5.90$$

$$H^+ + F^- \rightleftharpoons HF \quad \log \beta_{011} = 2.97$$

$$H^+ + 2F^- \rightleftharpoons HF_2^- \quad \log \beta_{012} = 3.56$$

The values for β_{101} and β_{011} were measured in our laboratory by separate potentiometric titrations using a fluoride ion-selective electrode. Although we were unable to determine a reliable stability constant for the formation of the second complex from the analysis of our Eu titration data, both the first and second constants have been reported recently by Becker and Bilal [9] at the same ionic strength of 1.0 M but in a different ionic medium (NaCl). When a correction of 0.2–0.3 for chloride complexation was applied to the log β_{101} value in reference [9], satisfactory agreement with our first constant was obtained, indicating that we could estimate β_{102} in $NaClO_4$ medium from the K_1/K_2 ratio measured in the NaCl medium. Using the K_1/K_2 ratio of 4.4 obtained by Becker and Bilal [9], a value of log β_{102} = 5.90 for a 1.0 M $NaClO_4$ medium was calculated and used in the analysis of our calorimetric data. The acid constants were taken from Martell and Smith's most recent evaluation [10], and β_{011} was verified in our laboratory by potentiometric titration.

From FNEWT calculations of the HF and EuF_x concentrations at each point in the titration, the contribution of HF to the measured heat was determined. The value of ΔH for HF formation used in these calculations was 11.43 kJ/mol. This result was obtained in separate experiments on our calorimeter system, with $1\sigma = 2.3\%$ uncertainty, and it agrees with the recommended value [10] to within 5%.

As described in the next section, it was necessary to include EuF_2^+ formation in the data analysis to obtain reasonable results for ΔH_{101}. Consequently, the equation

$$\Delta Q_{\mathbf{EuF}_x} = (\Delta H_{101})(\Delta n_{\mathbf{EuF}}) + (\Delta H_{102})(\Delta n_{\mathbf{EuF}_2})$$

was solved for the values of ΔH_{101} and ΔH_{102} at each point in the titration. Here, $\Delta Q_{\mathbf{EuF}_x}$ is the empirical titration heat corrected for heat-of-dilution and HF formation, and $\Delta n_{\mathbf{EuF}}$ and $\Delta n_{\mathbf{EuF}_2}$ are the FNEWT-calculated change in moles of EuF_2^+ and EuF_2^+, respectively. The two-parameter equation was solved via a weighted nonlinear regression analysis utilizing the method described by Wentworth [11].

All errors given in this work are 1σ standard deviations and are propagated uncertainties inherent in the calorimeter measurement of calibration and titrant-addition temperatures only [1]. Uncertainties in the stability constants, concentrations, etc. utilized by the theoretical FNEWT calculations have not been factored into the error analysis. Consequently, the instrumental errors quoted represent minimum errors associated with these experiments.

Results and Discussion

If only the monofluoro-europium complex is considered in the data reduction, the resulting values of ΔH_{101} are not satisfactory. These results are summarized in Fig. 1 for the three titrant concentrations. As shown in the figure, ΔH_{101} is not constant but

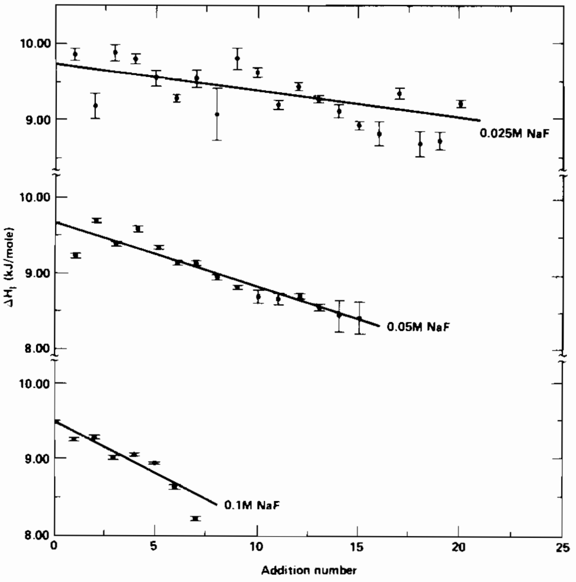

Fig. 1. The variation of ΔH_{101} with addition number at three titrant concentrations assuming only HF and EuF^{2+} formation in the solution speciation calculations.

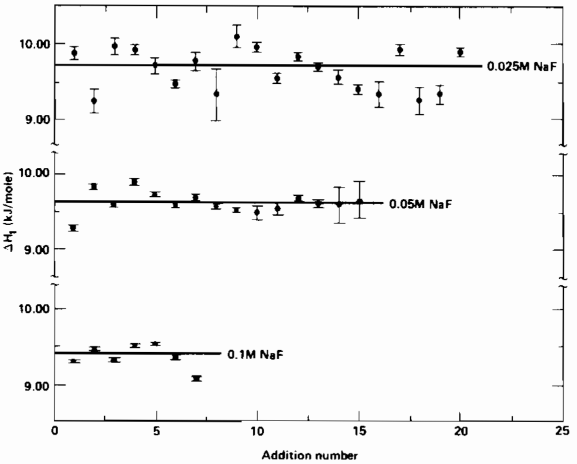

Fig. 2. The variation of ΔH_{101} with addition number at three titrant concentrations after allowing HF, EuF^{2+}, and EuF$_2^+$ formation in the speciation calculations.

rather is observed to be a decreasing function of titrant addition for all concentrations investigated. (Only 7 points are given for the 0.1 M NaF experiments because EuF$_3$ precipitation commenced at addition no. 8 under these conditions.)

When EuF$_2^+$ formation is taken into account in the data analysis, a constant value of ΔH_{101} = (9.61 ± 0.03) kJ/mol is found for the instrumentally-weighted average of all of the data points determined from the titrations at the different fluoride concentrations (Fig. 2). Apparently, the inclusion of the second complex is important even though the fraction of the metal complexed as EuF$_2^+$ is only a few percent of that complexed as EuF^{2+} at the end of any given titration. The bivariate fit [11] used to extract the least-squares value of ΔH_{101} from our experiments of course also determined a value for ΔH_{102}. However, since only a small amount of EuF$_2^+$ is formed during a titration, the error associated with ΔH_{102} is relatively large. Further, the magnitude of ΔH_{102} is very dependent upon the K_1/K_2 ratio for EuF$_x$ complexation. In contrast, the computed value of ΔH_{101} is relatively insensitive to the value of β_{102} since, at any point in the titration, the concentration of EuF$_2^+$ is small compared to that of EuF^{2+}. To illustrate this point, our result for ΔH_{101} would change by only 5% if K_1/K_2 was changed from 4.4 to 2.0. (This latter value was measured by Aziz and Lyle [12] in work at $\mu = 0.5$ M (NaClO$_4$).) The result for ΔH_{102}, however, changes sign from approximately −5 kJ/mol to +8 kJ/mol with the same change in K_1/K_2. The effect of a realistic error in the value of log β_{101} on the magnitude of ΔH_{101} is considerably less than that of the assumed K_1/K_2 ratio. For example, if we allow a variation in log β_{101} of ±0.02, the average value of ΔH_{101} changes by 1.4%.

Our reported value for ΔH_{101} is a factor of 4.0 lower than the presently accepted literature value [2]. A study at $\mu = 1.0$ M (NaClO$_4$) [13] by the solvent extraction technique lists a value of 38 kJ/mol for ΔH_{101}, in apparent agreement with reference [2]. However, our analysis of the temperature dependence of the β_{101} data presented in reference [13] calculates ΔH_{101} = 19 kJ/mol. This result is a value intermediate between that of reference [2] and the present work.

Problems with the literature data for lanthanide–fluoride interactions have been noted previously by Hefter [14]. In reviewing fluoride complexation with a wide variety of metals, he noted a linear correlation of ΔS_{101} with the parameter $Z_+/r_+ + r_-$, which describes the coulombic interaction of a cation and an anion. For this parameter, Z_+ is the charge on the metal, and r_+ and r_- are the ionic radii of the metal and fluoride ions, respectively. Since the fluoride ion behaves as a hard base because it is not easily polarized, fluoride interactions with metal ions should be well-described by electrostatic theories and should correlate with parameters such as $Z_+/r_+ + r_-$.

For the 15 metal monofluoride complexes considered by Hefter for his fit, we calculate a linear correlation coefficient $r = 0.92$. As Hefter points out, if the existing lanthanide literature data are also included, the correlation disappears; in fact, r degrades to 0.64. The predicted value for ΔS_{101} of EuF^{2+} from Hefter's correlation is (88 ± 27) J/deg mol. Using the value log $\beta_{101} = 3.27$ to calculate ΔG_{101}, the previously reported [2] value of ΔH_{101} gives rise to a value of ΔS_{101} of 192 J/deg mol. In comparison, using the same ΔG_{101} and the value of ΔH_{101} reported here, the calculated value of ΔS_{101} is

95 J/deg mol, which agrees quite well with the established correlation. It would be unexpected for the entropy derived for a lanthanide–fluoride complex to be poorly described by electrostatic theories since the bonding of lanthanide ions can be considered to be very strongly electrostatic.

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