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Enthalpies of Formation of the Monofluorolanthanide Complexes†

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The enthalpies of formation of the monofluoro complexes of 13 lanthanide elements and yttrium have been measured in aqueous solution at 25 °C and an ionic strength of 1.0 M by titration calorimetry. Our results for YF^{2+} compare well with previously reported determinations obtained from temperature-coefficient variations of potentiometric data. The enthalpies of complexation for LnF^{2+} were found to be endothermic for all lanthanide metals studied and show considerably less variation with increasing atomic number than previous studies. Our values for ΔH_{101} for the lanthanides are much less endothermic than the earlier determinations and appear to agree well with electrostatic models which correlate entropies for fluoride complex formation with charge/radius ratios. These results indicate that the coordination behavior of the fluoride ion is more similar to that of the acetate ion than was previously thought.

Introduction

Complexation reactions of the fluoride ion are of interest because of its small size and unique electronic properties. Because the fluoride anion is difficult to polarize, its reactions are dominated by electrostatic factors and it is therefore a model anion for hard-acid/hard-base reactions in aqueous solutions. Fluoride complexes thus offer fundamental tests of electrostatic bonding theories with minimal contributions from the complications associated with covalent bonding.[1,2]

To test the performance of a new calorimeter system, we decided to remeasure the enthalpies of complexation of the lanthanide–fluoride systems reported by Walker and Choppin.[3] Fluoride electrode measurements confirmed the ΔG values reported by Walker and Choppin, but our measurements of ΔH_{101} gave values that were factors of 2–4 less endothermic. In addition, our results disagreed with the enthalpy data of Moulin et al.,[4] who reported exothermic values for Eu, Gd, and Tb derived from temperature variations of stability constants.

A problem with the literature thermodynamic values for lanthanide–fluoride interactions has been previously noted in a review article by Hefter.[1] He correlated certain thermodynamic parameters for a number of aqueous hard-cation–fluoride complexes in terms of Coulombic interactions. The ion–ion electrostatic interaction potential, V, can be formulated as

$$V = -[Z_+Z_-e^2/\epsilon r]$$

where Z_+ is the charge on a cation of radius r_+, Z_- is the charge on an anion of radius r_-, e is the elementary charge, ϵ is the dielectric constant of the medium, and $r = r_+ + r_-$. This equation does not suffer from the use of arbitrary single-ion radii and is likely valid for inner-sphere, "contact" ion pairs.

Hefter observed that no correlation of ΔH_{101} with metal ion properties existed for metal–fluoride complexes due to the small enthalpy changes associated with the overall process of complex formation in aqueous solution. However, a rough linear relationship was found when the most reliable ΔS_{101} data were plotted versus Z_+/r. Hefter excluded Walker and Choppin's lanthanide–fluoride data from his correlation since he considered them to be anomalously high.

This work reports a redetermination of the enthalpies of complexation of the lanthanide–fluoride and yttrium–fluoride complexes that results in new values which give much better agreement with electrostatic models of fluoride bonding.

Experimental Section

Metal stock solutions of yttrium and 13 lanthanide elements were prepared by dissolving ≥99.99% pure oxide powders in $HClO_4$. These solutions were filtered, adjusted to pH 2–3 with $HClO_4$, and analyzed by complexometric titration with EDTA. Metal ion solutions (0.03–0.04 M) for calorimetric determinations were prepared from aliquots of the stock solutions and were adjusted to a constant ionic strength ($\mu = 1.00$ M) at pH 2–3 with $NaClO_4$. Hydrogen ion concentrations of the working solutions were measured with a combination glass electrode that had been calibrated with solutions of known H^+ concentration at $\mu = 1.00$ M.

The fluoride titrants used in this work were 0.025 and 0.100 M NaF solutions prepared at pH 6.5–7.0 and $\mu = 1.00$ M ($NaClO_4$). The titrant solutions were prepared gravimetrically from reagent NaF that had been purified by the method of Lingane.[5] Class A volumetric glassware and analytical reagent-grade quality (or better) materials were used throughout this work.

The titration calorimeter utilized in these experiments operates in an adiabatic mode and is similar in principle to the instrument described by Caceci and Choppin.[6] The operation, sensitivity, and accuracy of the calorimeter have been reported elsewhere.[7] All titration calorimetry experiments were performed at a temperature of 25.00 ± 0.0003 °C, and the results reported here represent two or more replicate experiments for each metal ion species.

The low pH values required to prevent hydrolysis of the M^{3+} ions in solution result in a competition between the metal cation and H^+ for the fluoride anion. Consequently, in these experiments, the heat generated or absorbed during a calorimetric titration must be partitioned between three distinct processes: $M^{3+} + F^-$ complexation reactions, the formation or disassociation of HF, and the heat of dilution of the titrant. The heat of dilution was measured by titrating a blank solution of 1.00 M $NaClO_4$ for each titrant concentration.

Concentrations of the reacting species of interest at each point in the titration are required to apportion the measured heat between the reactions of fluoride with metal ions (formation of MF^{2+} and MF_2^+) and with hydrogen ions (formation of HF and HF_2^-). The concentrations of the various species were calculated with our program FNEWT, which uses the Newton–Raphson method to iteratively calculate solution speciation at points in the titration.[8] Protonation constants for HF required as input for FNEWT were those reported by Martell and Smith ($\log \beta_{011} = 2.97$, $\log \beta_{012} = 3.56$).[9] With the exception of Eu, the metal stability constants reported by Walker and Choppin were used in the speciation calculations.

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Table I. Thermodynamic Parameters for $M^{3+} + F^- \rightleftarrows MF^{2+}$ at 25 °C and μ = 1.0 M ($NaClO_4$)

metal	$-\Delta G_{101}$,[a] kJ/mol	ΔH_{101}, kJ/mol	ΔS_{101}, J/(mol K)
La	15.2 ± 0.92	12.1 ± 0.47	91.7 ± 3.5
Pr	17.2 ± 1.4	14.5 ± 0.26	106 ± 4.7
Nd	17.6 ± 1.4	13.5 ± 0.30	104 ± 4.9
Sm	17.8 ± 0.54	10.8 ± 0.49	95.9 ± 2.4
Eu	18.7 ± 0.07[b]	9.61 ± 0.03	94.8 ± 0.3
Gd	18.9 ± 1.7	9.22 ± 0.07	94.4 ± 5.9
Tb	19.6 ± 0.96	9.30 ± 0.09	96.8 ± 3.3
Dy	19.8 ± 1.8	9.27 ± 0.13	97.4 ± 5.9
Ho	20.1 ± 0.79	10.0 ± 0.05	101 ± 2.5
Er	20.2 ± 0.59	10.6 ± 0.12	103 ± 2.1
Tm	20.3 ± 0.63	10.8 ± 0.05	104 ± 2.1
Yb	20.4 ± 1.4	11.2 ± 0.37	106 ± 5.0
Lu	20.6 ± 1.5	11.8 ± 0.14	109 ± 5.0
Y	20.6 ± 1.8	9.27 ± 0.07	100 ± 6.3

[a] Reference 3 except as indicated. The indices "101" refer to the number of atoms of metal, hydrogen, and ligand, respectively, in the complex. Thus "101" indicates the reaction $M + F \rightleftarrows MF$, "011" indicates $H + F \rightleftarrows HF$, etc. [b] Reference 8.

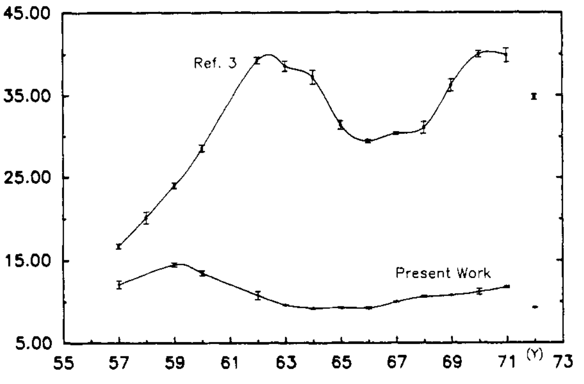

Figure 1. Variation of the enthalpy of formation of monofluorolanthanide complexes with lanthanide atomic number. The earlier results of Walker and Choppin[3] are shown for comparison with the present measurements.

Becker and Bilal recently reported lanthanide–fluoride stability constants measured in 1.0 M NaCl.[10] When a correction is made for complexation by chloride, their fluoride stability constants agree with the values of Walker and Choppin. We also remeasured a number of lanthanide–fluoride stability constants by potentiometric titration using a fluoride ion-selective electrode. In all cases, including Eu, our β_{101} constants agreed with Walker and Choppin's values to within ±0.1 log unit. We have chosen to use our measured Eu stability constant to remain consistent with our previously reported study of europium–fluoride complex formation.[8]

The HF contribution to the heat of reaction was calculated using concentrations generated by the FNEWT program and a ΔH_{011} value of 11.43 kJ/mol. Separate calorimeter experiments gave this result, with an uncertainty (1σ) of ±2.3%, and its agrees with an existing literature value to within 5%.[11]

More specific detail on experimental analysis and error propagation has been given elsewhere.[7,8] All errors reported in this work represent 1σ standard deviation and reflect only the uncertainties in the calorimeter temperature measurements. The errors reported therefore represent minimum values associated with these experiments.

Results

New measurements of ΔH_{101} for the reaction of fluoride with 13 lanthanide elements and yttrium are presented in Table I. The entropy values have been calculated from these data and the stability constant values of Walker and Choppin, except for Eu as noted above. Figure 1 shows a plot of our measured ΔH_{101} values compared with those reported by Walker and Choppin. Our data are consistently less endothermic and show much less variation with atomic number. Since our values of ΔG_{101} are identical with those of Walker and Choppin, our results for ΔS_{101} are smaller by factors of 1.5 to 2 due to our smaller values of ΔH_{101}.

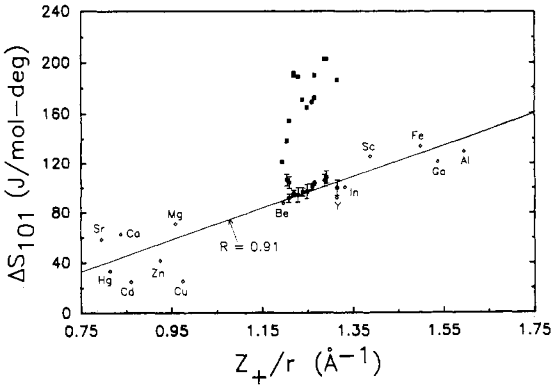

Figure 2. Correlation of formation entropy with Coulomb attraction for metal-monofluoride species [from Hefter[1]]. The line represents the best fit for all data, including the present study (● with error bars) but excluding the entropy values of Walker and Choppin, which are shown for comparison (■).

Enthalpy measurements for the complexation of yttrium with fluoride have been reported from temperature–coefficient methods of potentiometric determinations in 0.5 M $NaClO_4$. Using a fluoride ion-selective electrode, Aziz and Lyle published a value for ΔH_{101} of 5.04 kJ/mol.[12] Paul and co-workers used the Fe(III)/Fe(II) half-cell method to measure the value of ΔH for the reaction $Y^{3+} + HF \rightleftarrows YF^{2+} + H^+$.[13] Using their reported equilibrium quotients and the HF ionization constants of Connick and Tsao,[14] we calculate a value of ΔH_{101} = 8.87 kJ/mol for YF^{2+}, which compares quite well with the value of 9.27 kJ/mol measured at μ = 1.0 M in the present work. All of these values are in marked disagreement with the value of 34.8 kJ/mol reported by Walker and Choppin.

Discussion

Figure 2 shows Hefter's plot of ΔS_{101} vs Z_+/r for 14 metal-fluoride complexes[1] along with the two sets of lanthanide fluoride data. Our data fit this correlation quite well (the linear correlation coefficient, R, changes by less than 0.01), and this fact, along with the agreement with the previously published yttrium data, confirms the validity of our results and further supports the highly ionic nature of metal–fluoride bonding.

In order to understand the effect that entropy changes have on lanthanide–fluoride complexation reactions, a number of contributions must be considered. For a metal–fluoride complexation reaction taking place in an aqueous solution, the reaction may be written as

$$M(H_2O)_x^{3+} + F(H_2O)_y^- \rightleftarrows MF(H_2O)_z^{2+} + (x + y - z)H_2O$$

The overall change in entropy is the sum of the molar entropies of the aquated metal and fluoride ions, the MF^{2+} complex, and the coordinated water molecules. This change in entropy is given by

$$\Delta S^\circ_{101} = S^\circ_{MF^{2+}(aq)} + (x + y - z)S^\circ_{H_2O} - S^\circ_{M^{3+}(aq)} - S^\circ_{F^-(aq)}$$

The overall stability constant of the complex formed by a hard, class A-type acceptor (such as a lanthanide metal) with a hard donor anion (such as fluoride) is typically accompanied by a large increase in entropy. Since our values for the enthalpy contribution from the complexation reaction are quite small and endothermic, the driving force for the reaction must be a large increase in entropy. In general, the enthalpy contribution is found to be small and exothermic for the formation of an outer-sphere complex (e.g., complexes formed by lanthanides with ligands such as chloride,

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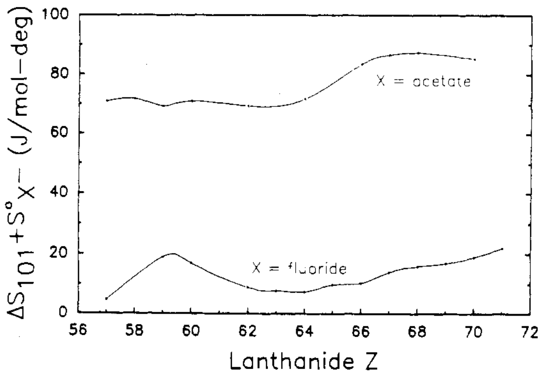

Figure 3. Comparison of the "corrected" entropy of formation of monofluorolanthanide and monoacetolanthanide complexes with lanthanide atomic number. The lower values for the fluoride complexes indicate a more hydrated complex.

nitrate, and thiocyanate). For an inner-sphere complex, the enthalpy contribution is small and endothermic (e.g., lanthanide complexes with mono- and polycarboxylate ligands).[15]

A comparison can be made between the complexation of the lanthanides with fluoride and their complexation with the acetate anion. Both ligands are relatively small and monodentate and form inner-sphere complexes. Because the fluoride anion is known to have a strong ordering effect on water, Walker and Choppin assumed that the dehydration of the metal ion would be the same whether complexed by either fluoride or acetate. They considered the effect of dehydration of the fluoride anion by subtracting the molar entropy contribution due to the ligand. Following this line of argument, by using the molar entropies at infinite dilution tabulated by Pitzer and Brewer[16] for the fluoride anion ($S^\circ_{\mathrm{F^-(aq)}} = -9.6$ J/(mol K)) and the acetate anion ($S^\circ_{\mathrm{CH_3COO^-(aq)}} = +87.1$ J/(mol K)), we can correct the observed values of ΔS_{101} for effects associated with hydration of the ligand. The sum of the relative entropy contribution of the metal–ligand complex and $(x + y - z)\ S^\circ_{\mathrm{H_2O}}$ can be estimated from a plot of $\Delta S_{101} + S^\circ_{\mathrm{X^-(aq)}}$ versus atomic number of the lanthanide metal, where $S^\circ_{\mathrm{X^-(aq)}}$ is the molar entropy of the fluoride or acetate anion.

Such a plot is shown in Figure 3, where it can be seen that $\Delta S_{101} + S^\circ_{\mathrm{CH_3COO^-(aq)}}$ is much more positive than $\Delta S_{101} + S^\circ_{\mathrm{F^-(aq)}}$. This can be interpreted to imply a more hydrated structure for the metal–fluoride complex than for the metal–acetate complex. This explanation is reasonable since the hydrophobic acetate anion should tend to disrupt the solvent structure around the complex. However, the fluoride anion is still capable of ordering water molecules through ion–dipole interactions on the side of the anion opposite the metal ion. The result should be a more ordered hydration structure for the fluoride complex than for the acetate complex.

Mesmer and Baes[17] speculated that the variation in the ΔS_{101} values with atomic number reported by Walker and Choppin might indicate a change in hydration for the lanthanide–fluoride complexes between Gd and Dy. However, our new data show little variation with atomic number and indicate no significant changes in the nature of the lanthanide–fluoride complex across the series.

Walker and Choppin compared their fluoride data with the analogous thermodynamic parameters measured for the interactions of lanthanides with acetate and glycolate anions. Some of their conclusions need revision in light of our new enthalpy measurements. In particular, marked differences between the fluoride anion and the acetate anion are no longer apparent. Corresponding values of ΔH_{101} and ΔS_{101} are now in much closer agreement (typically within 50%), and the pronounced differences between fluoride and acetate in the shapes of the plots of ΔH_{101} and ΔS_{101} versus atomic number no longer exist.

Conclusions

The new measurements of the thermodynamic parameters of the lanthanide–fluoride complexation reactions are in marked disagreement with the previously reported literature values. However, the new entropy data agree well with a correlation derived from a purely electrostatic model of metal–fluoride complexes. Our measurements for yttrium, measured under the same conditions, do agree well with published enthalpy values. The new enthalpy and entropy data indicate that the coordination of the lanthanides with fluoride is more similar to their interactions with acetate than was previously suspected.

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Registry No. $\mathrm{LaF^{2+}}$, 18989-24-7; $\mathrm{PrF^{2+}}$, 18946-71-9; $\mathrm{NdF^{2+}}$, 18946-53-7; $\mathrm{SmF^{2+}}$, 18946-55-9; $\mathrm{EuF^{2+}}$, 18946-56-0; $\mathrm{GdF^{2+}}$, 18946-57-1; $\mathrm{TbF^{2+}}$, 18946-58-2; $\mathrm{DyF^{2+}}$, 18946-59-3; $\mathrm{HoF^{2+}}$, 18946-60-6; $\mathrm{ErF^{2+}}$, 18946-61-7; $\mathrm{TmF^{2+}}$, 18946-62-8; $\mathrm{YbF^{2+}}$, 18946-63-9; $\mathrm{LuF^{2+}}$, 18946-64-0; $\mathrm{YF^{2+}}$, 18946-65-1.

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