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Complexation of Lanthanides with Nitrate at Variable Temperatures: Thermodynamics and Coordination Modes

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Complexation of neodymium(III) with nitrate was studied at variable temperatures (25, 40, 55, and 70 °C) by spectrophotometry and microcalorimetry. The $NdNO_3^{2+}$ complex is weak and becomes slightly stronger as the temperature is increased. The enthalpy of complexation at 25 °C was determined by microcalorimetry to be small and positive, 1.5 ± 0.2 kJ·mol^{-1}, in good agreement with the trend of the stability constant at variable temperatures. Luminescence emission spectra and the lifetime of Eu(III) in nitrate solutions suggest that inner-sphere and bidentate complexes form between trivalent lanthanides (Nd^{3+} and Eu^{3+}) and nitrate in aqueous solutions. A specific ion interaction approach was used to obtain the stability constants of $NdNO_3^{2+}$ at infinite dilution and variable temperatures.

1. Introduction

Although a considerable number of stability constants of lanthanide and actinide complexes with inorganic and organic ligands have been published,[1] the coordination chemistry of lanthanides and actinides remains an active and challenging subject of study at both fundamental and applied levels. At the fundamental level, many aspects concerning the nature of complexes, including the hydration number, coordination modes, and the nature of bonding (e.g., inner-sphere vs outer-sphere), are not fully understood.[2] At the applied level, recent activities in the environmental management of nuclear wastes have stimulated significant interest in the coordination chemistry of lanthanides and actinides in complicated matrices and under conditions relevant to nuclear wastes. For example, because the temperature of the high-level nuclear wastes in storage tanks and in the geological repository could be significantly higher than the ambient temperature, thermodynamic data on the complexation of lanthanides and actinides at elevated temperatures are needed in order to predict the behavior of lanthanides and actinides in waste processing or disposal. Currently, the majority of thermodynamic data for lanthanides and actinides are determined at or near 25 °C. Stability constants at elevated temperatures are very scarce. Even for 25 °C, thermodynamic parameters other than stability constants, for example, enthalpy of complexation, are rarely available.[1,3−5]

It is known that nitrate is a weak complexant for metal cations in aqueous solutions. However, it is present in high concentrations in the process of spent nuclear fuel reprocessing as well as in nuclear wastes. As a result, complexation with nitrate could alter the speciation and affect the chemical behavior of lanthanides and actinides in the reprocessing processes. In addition, concentrated nitrate is often used as the “background” electrolyte in complexation studies. Consequently, correction for the complexation with nitrate must be made in order to calculate the stability constants and enthalpy of lanthanide and actinide complexes with other ligands. Therefore, thermodynamic parameters of lanthanide and actinide nitrate complexes should be known. In particular, stability constants at elevated temperatures and the

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enthalpy of complexation should be determined since spent fuel reprocessing and waste treatment are usually operated at elevated temperatures.

There have been a number of studies[6−20] to determine the stability constants of lanthanide(III) complexes with nitrate in aqueous solutions. However, few were conducted at temperatures higher than 25 °C, and the data at 25 °C are scattered. Furthermore, the nature of the nitrate complex (e.g., outer- or inner-sphere) and the coordination mode (e.g., mono- or bidentate) are still open for discussion. In this work, we have determined the stability constant of the 1:1 Nd(III)/nitrate complex, $NdNO_3^{2+}$, at temperatures from 25 to 70 °C by spectrophotometry and the enthalpy of complexation at 25 °C by microcalorimetry. In addition, when Eu(III) was used as a chemical analog to Nd(III), luminescence emission spectra and the lifetime of Eu(III) in nitrate solutions were studied to help probe the coordination mode of nitrate in the Nd(III)/nitrate complex, and lanthanide(III)/nitrate complexes in general.

2. Experimental Section

2.1. Chemicals. All chemicals were reagent-grade or higher. Milli-Q water was used in the preparations of all solutions. Stock solutions of Nd(III) perchlorate or Eu(III) perchlorate were prepared by dissolving Nd_2O_3 or Eu_2O_3 in perchloric acid (70%, Aldrich). The concentrations of lanthanides and perchloric acid in the stock solutions were determined by EDTA complexometry[21] and Gran's titration,[22] respectively. A stock solution of sodium nitrate was prepared by dissolving appropriate amounts of sodium nitrate solid in water. The ionic strength of all working solutions was adjusted to 1.0 $mol \cdot dm^{-3}$ $Na(ClO_4/NO_3)$ at 25 °C. All of the molar concentrations in this paper are referred to 25 °C.

2.2. Spectrophotometric Titrations at Variable Temperatures. Absorption spectra of Nd(III) (550−600 nm, 0.1 nm interval) were collected on a Varian Cary-5G spectrophotometer equipped with sample holders that were maintained at constant temperatures. Ten-millimeter quartz cells were used. Details of the experimental setup were provided elsewhere.[23] Multiple titrations with different concentrations of Nd(III) were performed. The initial concentrations of Nd(III) in the cells ranged from 0.08 to 0.10 $mol \cdot dm^{-3}$. In each titration, appropriate aliquots of the titrant (1.00 $mol \cdot dm^{-3}$ $NaNO_3$) were added into the cell and mixed thoroughly (for 1−2 min) before the spectrum was collected. The mixing time was found to be sufficiently long for the complexation to complete. Usually, 10−15 additions were made, generating a set of 10−15 spectra in each titration. The stability constant of the Nd(III)/nitrate complex (on the molarity scale) was calculated by nonlinear least-squares regression using the Hyperquad program.[24]

2.3. Microcalorimetry. Calorimetric titrations were conducted with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp.) at 25 °C. Procedures and results of the calibration of the calorimeter were provided elsewhere.[23]

To maximize the formation of the Nd(III)−nitrate complex, the titrations were conducted with 0.900 mL of 1.0 $mol \cdot dm^{-3}$ $NaNO_3$ in the cell, titrated with solutions of $Nd(ClO_4)_3$. Both the cell and titrant solutions contain 0.001 $mol \cdot dm^{-3}$ $HClO_4$. Multiple titrations with different concentrations of $Nd(ClO_4)_3$ (0.0375, 0.050, and 0.075 $mol \cdot dm^{-3}$) were performed to reduce the uncertainty of the results. In a typical titration, n additions of the titrant were made (usually $n = 40-50$), resulting in n experimental values of the total heat generated in the reaction cell ($Q_{ex,j}$, $j = 1-n$). These values were corrected for the heats of dilution of the titrant ($Q_{dil,j}$) that were determined in separate runs. The net reaction heat at the jth point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_{Nd}, C_H, and $C_{nitrate}$), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. A least-squares minimization program, Letagrop,[25] was used to calculate the enthalpy of complexation of Nd(III) with nitrate.

2.4. Luminescence Spectroscopy. Luminescence emission spectra and the lifetime of Eu(III) in aqueous solutions ([Eu(III)] = 0.0202 $mol \cdot dm^{-3}$, [nitrate] = 0−0.90 $mol \cdot dm^{-3}$) were acquired on a HORIBA Jobin Yvon IBH FluoroLog-3 fluorometer adapted for time-resolved measurements. Ten-millimeter quartz cells were used. A submicrosecond Xenon flash lamp (Jobin Yvon, 5000XeF) was the light source and was coupled to a double grating excitation monochromator for spectral selection. The input pulse energy (100 nF discharge capacitance) was about 50 mJ, and the optical pulse duration was less than 300 ns at fwhm. A thermoelectrically cooled single-photon detection module (HORIBA Jobin Yvon IBH, TBX-04-D) that incorporates a fast risetime PMT, a wide bandwidth preamplifier, and a picosecond constant fraction discriminator was used as the detector. Signals were acquired using an IBH Data Station Hub, and data were analyzed using the commercially available DAS 6 decay analysis software package from HORIBA Jobin Yvon IBH. The goodness of fit was assessed by minimizing the reduced function, χ^2, and visually inspecting the weighted residuals. Each trace contained at least 10 000 points, and the reported lifetime values resulted from at least three independent measurements.

3. Results

3.1. Stability Constants of $NdNO_3^{2+}$ at Variable Temperatures. Figure 1 shows the absorption spectra of two representative titrations at 25 and 70 °C. The absorption band around 575 nm corresponds to the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition of Nd(III) that is sensitive to the coordination environment.[26−29] At each temperature, the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition was slightly intensified and red-shifted as the con-

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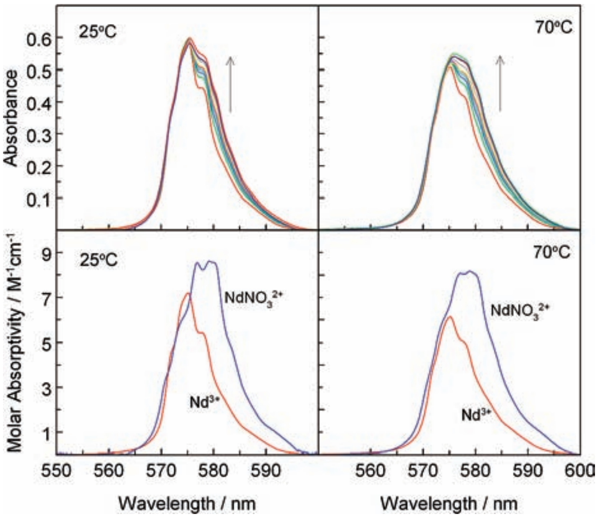

Figure 1. Representative spectrophotometric titrations of Nd(III)−nitrate complexation. I = 1.0 mol·dm^{-3} Na(ClO_4/NO_3). Upper figures show normalized absorption spectra of the titrations at 25 and 70 °C. Initial solution in cuvette: 2.50 mL, 0.0832 mol·dm^{-3} Nd(ClO_4)$_3$/0.100 mol·dm^{-3} $HClO_4$. Titrant: 1.00 mol·dm^{-3} $NaNO_3$. Lower figures show calculated molar absorptivity of Nd^{3+} and $NdNO_3^{2+}$.

Table 1. Complexation of Nd(III) with Nitrate at Different Temperatures, $K_M = [NdNO_3^{2+}]/([Nd^{3+}][NO_3^-])$ in Molarity[a]

t, °C	I, mol·dm^{-3}	method	K_M	log K_M	ΔH, kJ·mol^{-1}	ΔS, J·K^{-1}·mol^{-1}	ref
25	1.0	sp	0.64	−0.19 ± 0.02	2.1 ± 0.5		p.w.
		cal			1.5 ± 0.2	1.4 ± 1.0	
40	1.0	sp	0.68	−0.17 ± 0.02			
55	1.0	sp	0.70	−0.15 ± 0.03			
70	1.0	sp	0.72	−0.14 ± 0.02			
25	1.0	sx		0.3			1, 7
25	2.0	cal	0.8		1.7	2	19
unknown	≤3.4	sp	1.24				18
20	4.2	sp	0.77				8
22	5	sx	1.06				20

[a] Methods: sp, spectrophotometry; cal, calorimetry; sx, solvent extraction. p.w., present work.

centration of nitrate was increased. Factor analysis by the Hyperquad program indicated that there are two absorbing species of Nd(III), and the spectra were best-fitted with the formation of $NdNO_3^{2+}$:

$$Nd^{3+} + NO_3^- = NdNO_3^{2+} \tag{1}$$

Deconvoluted spectra of Nd^{3+} and $NdNO_3^{2+}$ at 25 and 70 °C are shown in the lower part of Figure 1. The spectra at 40 and 55 °C are not shown, but the trends in the spectra features are similar at each temperature.

The formation constants of $NdNO_3^{2+}$ at 25, 40, 55, and 70 °C were calculated and listed in Table 1. Other values at different ionic strengths at 20−25 °C from the literature are also listed for comparison. The uncertainties of log K_M in the table are "composite" values obtained by taking into consideration the statistic deviations of multiple titrations at each temperature and are about 2 times larger than the standard deviations calculated by Hyperquad. The latter are usually quite small (±0.01 or smaller) and probably unrealistic. Data in Table 1 indicate that the complexation of Nd(III) with nitrate is quite weak. However, a clear trend is shown that the complexation is enhanced as the temperature is increased. The linearity of the van't Hoff plot (log K vs. 1/T, Figure 2) suggests that the enthalpy of complexation can be assumed constant in the temperature range (25−70 °C). From the slop of the linear fit (weighted by the uncertainties), the enthalpy of complexation for the temperature range was calculated to be 2.1 ± 0.5 kJ·mol^{-1}.

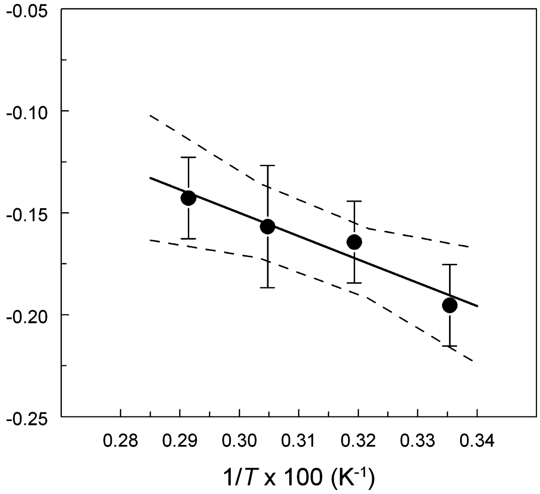

Figure 2. log K vs 1/T for Nd(III)/nitrate complexation. I = 1.0 mol·dm^{-3} Na(ClO_4/NO_3). Solid line, weighted (by uncertainty) linear fit; dashed lines, upper and lower limits of the confidence band at the 95% level.

To allow a comparison of stability constants at different temperatures, the constants in molar units should be corrected to obtain those in molal units.[3,4] However, the correction was smaller than or at most comparable to the uncertainties of the experimental values of $\log_{10} K_M$ ($NdNO_3^{2+}$). Therefore, we have elected to assume $\log_{10} K_M \approx \log_{10} K_m$ in this work.

3.2. Direct Determination of Enthalpy of Complexation at 25 °C by Calorimetry. Figure 3 shows the data from calorimetric titrations, in the form of the accumulated reaction heat as a function of the volume of the titrant. Results with three titrants of different concentrations of Nd(ClO_4)$_3$ (0.0375, 0.050, and 0.075 mol·dm^{-3}) are shown. Using these data in conjunction with the stability constant obtained by spectrophotometry, the enthalpy of complexation (eq 1) was calculated to be 1.5 ± 0.2 kJ·mol^{-1} at 25 °C. This value is in good agreement with the value of 2.1 ± 0.5 kJ·mol^{-1} obtained by the van't Hoff plot and consistent with the observed trend that the complexation of Nd(III) with nitrate is slightly enhanced at elevated temperatures. With the stability constant and enthalpy of complexation, the entropy of complexation (eq 1) was calculated to be 1.4 ± 1.0 J·K^{-1}·mol^{-1} at 25 °C.

3.3. Emission Spectra and Lifetime of the Luminescence of Eu(III). Figure 4 shows the luminescence emission spectra of Eu(III) in aqueous nitrate solutions. The spectra contain features originating from electronic transitions from

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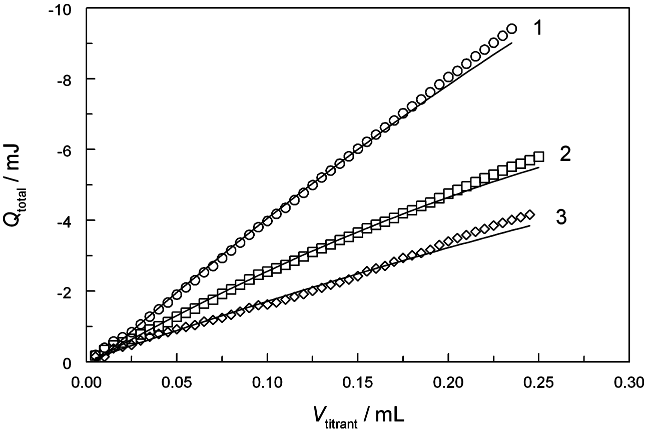

Figure 3. Calorimetric titrations of Nd(III)−nitrate complexation, $t = 25$ °C, $I = 1.0$ mol·dm^{-3} Na(ClO$_4$/NO$_3$). Cup solution: 0.900 mL 1.0 mol·dm^{-3} NaNO$_3$/0.001 mol·dm^{-3} HClO$_4$. Titrant: Nd(ClO$_4$)$_3$ in 0.001 mol·dm^{-3} HClO$_4$; C_{Nd} (mol·dm^{-3}) = 0.075 (1), 0.050 (2), 0.0375 (3). Symbols, experimental; lines, calculated.

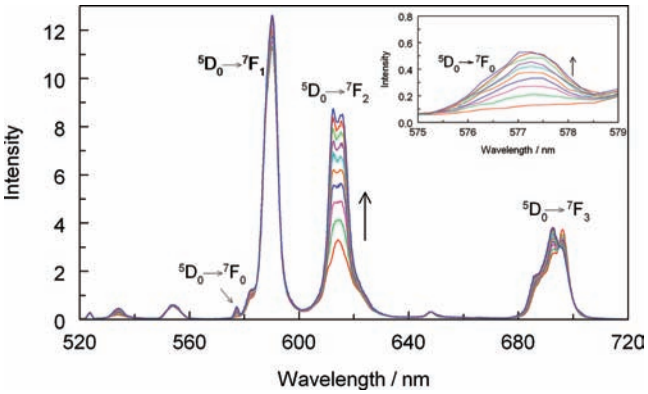

Figure 4. Fluorescence emission spectra of Eu(III)/nitrate systems. $I = 1.0$ mol·dm^{-3} Na(ClO$_4$/NO$_3$). [Eu(III)]$_{total}$ = 0.0202 mol·dm^{-3}, [H$^+$] = 0.100 mol·dm^{-3}, [nitrate]$_{total}$ from 0 to 0.900 mol·dm^{-3}. Excitation wavelength: 394 nm.

the lowest excited state, $^5D_0$, to the ground-state manifold, ^7F_J ($J = 0-3$). As the concentration of nitrate was increased from 0 to 0.9 mol·dm^{-3}, changes occurred in the transitions of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_3$, indicating the perturbation of the primary coordination sphere of Eu(III) by nitrate. In particular, the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (around 615−620 nm) increased significantly with the increase of the nitrate concentration. Contrarily, the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition (around 590−600 nm) is little affected because it is a magnetic dipole transition and not sensitive to the coordination environment of the fluorescent ion.[30] In fact, this band is often used as the internal standard for intensity comparison.

The luminescence decay of Eu(III) is shown in Figure 5 by two sets of data for solutions with $C_{nitrate} = 0$ and 0.90 mol·dm^{-3}. The decay pattern is fitted with a single exponential function, and the lifetime (τ_{H_2O}) is thus calculated. The lifetime of all Eu(III) solutions with different $C_{nitrate}$ values is summarized in Table 2. The values are in good agreement with those previously observed for Eu(aq)$^{3+}$ (108, 113 μs)[13,31] and that estimated for EuNO$_3$(aq)$^{2+}$ (159 μs).[13]

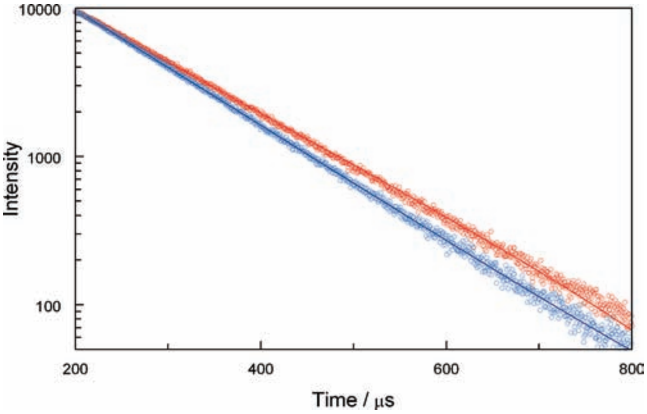

Figure 5. Decay of Eu(III) luminescence (at 615−620 nm) in aqueous solutions. $I = 1.0$ mol·dm^{-3} Na(ClO$_4$/NO$_3$). [Eu(III)]$_{total}$ = 0.0202 mol·dm^{-3}, [H$^+$] = 0.100 mol·dm^{-3}, [nitrate]$_{total}$ = 0 (blue) and 0.90 mol·dm^{-3} (red). $\lambda_{ex} = 394$ nm.

Table 2. Luminescence Lifetime ($C_{Eu} = 0.0202$ mol·dm^{-3}, $I = 1.0$ mol·dm^{-3} Na(ClO$_4$/NO$_3$), $\lambda_{ex} = 394$ nm, $\lambda_{em} = 615-620$ nm)

C_{NO_3}, mol·dm^{-3}	τ (±4), μs	$n_{H_2O,exp}$ (±0.5)	$n_{NO_3,b}$[a] (bidentate)	$n_{NO_3,m}$[a] (monodentate)
0	111	8.75	0	0
0.1	115	8.43	0.16	0.32
0.2	115	8.43	0.16	0.32
0.3	119	8.12	0.31	0.63
0.4	120	8.05	0.35	0.70
0.5	122	7.91	0.42	0.84
0.6	123	7.84	0.46	0.92
0.7	125	7.70	0.52	1.04
0.8	122	7.91	0.42	0.84
0.9	126	7.63	0.56	1.12

[a] $n_{NO_3,b}$ and $n_{NO_3,m}$ are the number of nitrate in the primary coordination sphere of Eu^{3+} obtained from $n_{H_2O,exp}$, assuming the nitrate is bidentate or monodentate, respectively.

It is evident that the luminescence lifetime becomes longer as $C_{nitrate}$ is increased, suggesting the number of water molecules in the primary coordination sphere of Eu^{3+} is reduced due to the complexation with nitrate. Using the relationship between the luminescence lifetime and the hydration number ($n_{H_2O} = 1.05 \times \tau_{H_2O}{}^{-1} - 0.7$, where τ_{H_2O} is in milliseconds),[31] the average number of water molecules in the primary coordination sphere of Eu^{3+} ($n_{H2O,exp}$) was obtained (Table 2). From $n_{H_2O,exp}$, the number of nitrates in the primary coordination sphere of Eu^{3+} can be calculated by assuming that the nitrate is either bidentate ($n_{NO_3,b}$) or monodentate ($n_{NO_3,m}$). These values are also listed in Table 2 and are discussed in section 4.3.

4. Discussion

4.1. Temperature Effect on Complexation. The band areas of the hypersensitive transition of Nd(III) ($^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$) were calculated by integrating the bands shown in Figure 1. After being normalized against the band area in the absence of nitrate, the band area is plotted against the ligand-to-metal ratio ($C_{nitrate}/C_{Nd}$) in Figure 6A. The plot indicates that the intensity of this transition was enhanced by the complexation of Nd(III) with nitrate in a similar manner at different temperatures, and that the enhancement is more significant at 70 °C than at 25 °C. On the basis of

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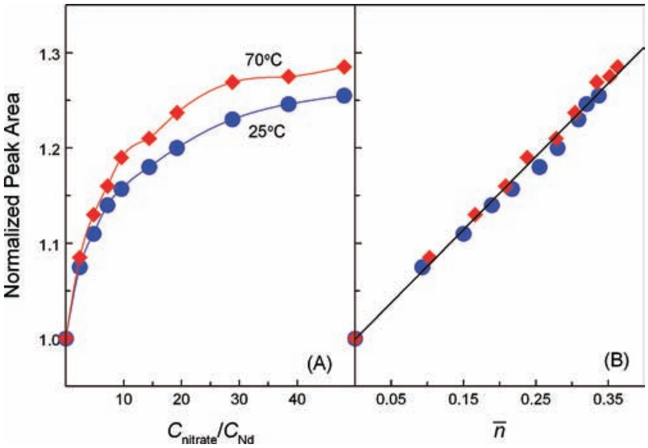

Figure 6. Normalized band area for the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd(III) vs $C_{\mathrm{nitrate}}/C_{\mathrm{Nd}}$ (A) and $\bar{n}$ (B) at 25 °C (●) and 70 °C (♦).

the generalization by Henrie et al.,[32] such a difference implies that, at the same ratio of $C_{\mathrm{nitrate}}/C_{\mathrm{Nd}}$, there are a greater number of coordinated nitrate ligands around Nd^{3+} at 70 °C than at 25 °C. In other words, the difference in the enhancement of intensity between 25 and 70 °C suggests that Nd(III)/nitrate complexation is stronger at higher temperatures. This is consistent with the trend in the thermodynamic constants shown in Table 1. Interestingly, if the normalized band area is plotted against the average number of nitrate ligands around Nd^{3+} ($\bar{n}_{NO_3}$, calculated with the stability constants at 25 and 70 °C in Table 1), the points for both temperatures fall onto a single straight line, indicating that the band area is proportional to $\bar{n}_{NO_3}$ no matter at what temperature (Figure 6B).

Jørgensen and Judd have concluded that the hypersensitive transitions in lanthanides are probably "pseudoquadrupole" in nature, and the hypersensitivity is believed to be due to Coulombic correlation of dipoles induced in the ligands by the transition quadrupole moment of the metal ion.[26−29] The changes in the absorption spectrum of Nd(III), the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition in particular, have been used to provide insight into the coordination environment of the Nd^{3+} ion in aqueous solutions.[32,33] For example, Choppin et al.[33] found that the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd(III) was greatly intensified as Nd(III) formed complexes with acetate. From the experimental data, the oscillator strengths for this transition were calculated to be 7.9×10^{-6} (for Nd^{3+}), 9.5×10^{-6} (for $Nd(OOCCH_3)^{2+}$), and 46×10^{-6} (for $Nd(OOCCH_3)_2^{+}$) in 2.0 mol·dm^{-3} $Na(ClO_4/NO_3)$.[33] In this work, we could calculate the oscillator strengths (f) of the Nd(III) species in nitrate systems from the integrated band areas of the deconvoluted spectra for $Nd(aq)^{3+}$ and $NdNO_3^{2+}$ (Figure 1). For the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition, $f = 9.53 \times 10^{-6}$ for $Nd(aq)^{3+}$ and 14.6×10^{-6} for $NdNO_3^{2+}$ at 25 °C and 9.05×10^{-6} for $Nd(aq)^{3+}$ and 14.8×10^{-6} for $NdNO_3^{2+}$ at 70 °C, in 1 mol·dm^{-3} $Na(ClO_4/NO_3)$. The oscillator strength for $NdNO_3^{2+}$ is higher than that for $Nd(aq)^{3+}$ at both temperatures, which seems to support the "pseudoquadrupole" mechanism of the intensity enhancement, because the $NdNO_3^{2+}$ species is expected to be more asymmetric than the $Nd(aq)^{3+}$ species, and the pseudoquadrupole transitions should be more intense in the former. In addition, the ratio of $f(NdNO_3^{2+})/f(Nd(aq)^{3+})$ is slightly larger at 70 °C (1.64) than that at 25 °C (1.53), suggesting that the complexation is slightly enhanced at higher temperatures.

4.2. Inner- vs Outer-Sphere Complexes. Whether the Nd(III)−nitrate complex is inner- or outer-sphere is another question that is still open for discussion. Outer-sphere complexes can be viewed as "solvent-separated" ion pairs in which the primary solvation sphere of the cation is not disturbed by the ligand, while inner-sphere complexes contain metal and ligand moieties in direct contact.[2] Actinide cations are known to form both inner- and outer-sphere complexes, and for labile complexes, it is often difficult to distinguish between these two types. Choppin et al. proposed to use thermodynamic parameters of complexation (enthalpy and entropy) to help evaluate inner-sphere vs outer-sphere complexation.[7] Because the primary solvation sphere is minimally perturbed by the ligand in outer-sphere complexes, little energy is spent on desolvation and little disordering occurs. As a result, outer-sphere complexation is often associated with exothermic enthalpy and negative entropy. In contrast, inner-sphere complexation often has endothermic enthalpy and positive entropy. Earlier data on the complexation of Eu(III) with nitrate appeared to suggest that the $EuNO_3^{2+}$ complex was outer-sphere, because the enthalpy and entropy of complexation were calculated to be −2.4 kJ·mol^{-1} and −2 J·K^{-1}·mol^{-1}, respectively.[7] However, later luminescence studies[13,14] provided evidence that $EuNO_3^{2+}$ had characteristics of inner-sphere complexation. From direct measurements of enthalpy with calorimetry and from the variation of stability constants with the temperature (25−70 °C), this study shows that both the enthalpy and entropy of $EuNO_3^{2+}$ complexation are small and positive (2 kJ·mol^{-1} and 1.4 J·K^{-1}·mol^{-1}, respectively). The small positive values of enthalpy and entropy from the present study do not strongly suggest that the $NdNO_3^{2+}$ complex is inner-sphere. However, on the basis of the changes in the absorption and luminescence spectra, we believe that both inner- and outer-sphere lanthanide(III) nitrate complexes exist in solutions. While methods such as solvent extraction[7] take into account both inner- and outer-sphere complexation, optical absorption and luminescence techniques used in this work and previous studies[13,14] probably probe only the inner-sphere complexation. This may explain the significant difference between the stability constant from ref 7 and that from this work at the same temperature (25 °C) and ionic strength (1.0 mol^{-1}·dm^{-3}; see Table 1).

The change in the $^5D_0 \rightarrow {}^7F_0$ transition (577−578 nm) of the Eu(III) luminescence spectra (Figure 4) is also very informative. Because both the initial and final states have $J = 0$ and its intensity is governed by the symmetry-related

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rule,[13] the change provides additional evidence that an inner-sphere complex forms between Eu^{3+} and nitrate. As the insert in Figure 4 shows, this transition was not observed when there was no nitrate in the Eu(III) solution. It appeared as nitrate was added, and its intensity increased as the concentration of nitrate was increased. This observation, consistent with those in previous luminescence studies,[13] suggests that the $Eu(aq)^{3+}$ ion probably possesses a center of inversion (e.g., as a mixture of hydrated ions with coordination numbers of 8 and 10) so that the $^5D_0 \rightarrow {}^7F_0$ transition is completely forbidden and that nitrate forms an "inner-sphere" complex with Eu(III) and destroys the center of inversion so that the transition becomes partially allowed.

4.3. Coordination Mode in the Lanthanide(III) Nitrate Complex. Data in the literature have shown that bidentate nitrato coordination is dominant in solid nitrato compounds of lanthanides such as $(NdCl(NO_3)_2)_2$[34] and $LaCl_2(NO_3)$(18-crown-6).[35] EXAFS studies have also shown that nitrate is bidentate in the complexes with Nd(III) and Lu(III) in aqueous solutions, with the N atom at about 2.5 Å from the metal atom.[36] However, quantum calculations suggest that, though bidentate coordination is preferred energetically when the first coordination shell is not crowded, monodentate and bidentate modes of binding become of similar energy when the first coordination shell is saturated. As the cation becomes smaller along the lanthanide series, the preference for monodentate nitrate binding may increase.[37]

Using Eu(III)/nitrate as a chemical analog to Nd(III)/nitrate, the luminescence lifetime data from this work help to clarify the coordination mode of nitrate in $NdNO_3^{2+}$. On one hand, the numbers of coordinating nitrate ($n_{NO_3,b}$ for bidentate and $n_{NO_3,m}$ for monodentate) are obtained from $n_{H_2O,exp}$ by assuming that the nitrate is either bidentate (each replacing two water molecules) or monodentate (each replacing one water molecule; Table 2). On the other hand, the average number of nitrates, $n_{NO_3,cal}$, can be calculated with a known stability constant of $EuNO_3^{2+}$ (Using $\log K^0$ ($EuNO_3^{2+}$) = 1.22 in the literature,[1] the SIT approach[3,4] and $\Delta\varepsilon = -(0.11 \pm 0.04)$[3,4] for reaction (1), $\log K$ ($EuNO_3^{2+}$) was calculated to be 0.11 at $I = 1.0$ mol•dm^{-3} $NaClO_4$ and $t = 25$ °C. A similar value of $\log K$ ($EuNO_3^{2+}$, 1 mol•dm^{-3}, 25 °C) = 0.09 was obtained by the analysis of the luminescence spectra in Fig. 4 using the Hyperquad program.[24]). A comparison between $n_{NO_3,cal}$ and $n_{NO_3,b}$ or $n_{NO_3,m}$ could reveal the coordination mode of nitrate in the complex−bidentate, monodentate, or mixed modes. As shown in Figure 7, data from this work suggest that nitrate binds Eu(III), and probably Nd(III) as well, in a bidentate mode in aqueous solutions.

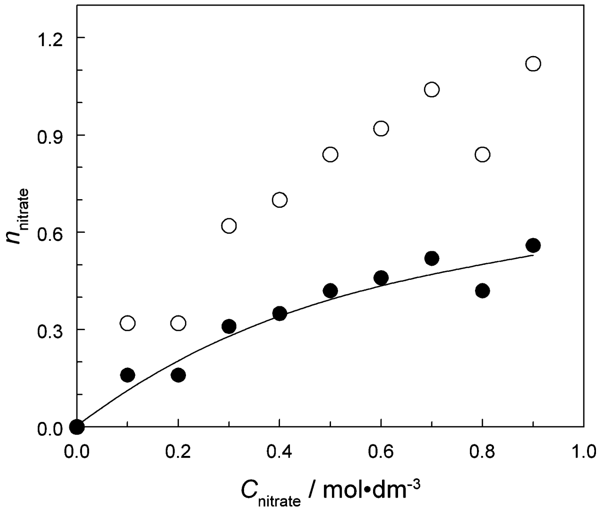

Figure 7. Comparison between the experimental values of $n_{NO_3,b}$ (●) or $n_{NO3,m}$ (○) from luminescence lifetime measurements and the calculated values of $n_{NO_3,cal}$ from speciation (solid line). $C_{Eu} = 0.0202$ mol•dm^{-3}, $I = 1.0$ mol•dm^{-3}, $t = 25$ °C.

4.4. Calculation of Stability Constants at Variable Temperatures to Infinitely Dilute Solutions: Analysis by the Specific Ion Interaction Approach (SIT). As preferred in common compilations of thermodynamic data, the standard state is defined as the infinitely dilute solution ($I = 0$ mol•dm^{-3}), with pure water as the solvent. The specific ion interaction (SIT) approach originated from the Brønsted−Guggenheim−Scatchard model has been used to calculate the equilibrium constants at zero ionic strength.[3,4] For reaction 1, the equilibrium constants at the standard state ($\log K^0_m$ in molality) are calculated by eq 2:

$$\log K_m + 6D = \log K^0 - \Delta\varepsilon I_m \qquad (2)$$

where $D = AI_m^{1/2}/(1 + Ba_jI_m^{1/2})$, the Debye−Huckel term used in SIT, and I_m is the ionic strength in molality. A and B are temperature-dependent constants, and a_j is an ion size parameter for the hydrated ion that is also temperature dependent. The change in the specific ion interaction parameters (kg•mol^{-1}) for reaction 1 at 25 °C are $\Delta\varepsilon = \varepsilon(NdNO_3^{2+}, ClO_4^-) - \varepsilon(Na^+, ClO_4^-) - \varepsilon(Nd^{3+}, ClO_4^-) = -(0.11 \pm 0.04)$.[3,4] For the calculation of $\log K^0_m$ at temperatures other than 25 °C, we have adopted the following approaches: (1) using $\log K_M^0$ (molarity) in Table 1 as $\log K_m^0$ (molality) without correction, as mentioned in previous sections; (2) using the values of A at different temperatures tabulated in the literature;[3,4] (3) using a constant value of $Ba_j = 1.5$ kg$^{1/2}$•mol$^{-1/2}$ for all temperatures, as recommended by the NEA review;[3,4] and (4) using the value of $\Delta\varepsilon$ at 25 °C for all temperatures, because the values at other temperatures were not known and the errors thus introduced are probably quite small, since the values of $(\varepsilon/T)_p$ are usually ≤ 0.005 kg•mol^{-1}•K^{-1} for temperatures below 200 °C.[3,4] In addition, the values of $(\varepsilon T)_p$ for the reactants and products may balance out each other so that $\Delta\varepsilon$ for many reactions remains approximately constant up to 100 °C.[38] The calculated $\log K_m^0$ values are 0.92 ± 0.04, 0.97 ± 0.04,

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1.03 ± 0.05, and 1.08 ± 0.04 at 25, 40, 55, and 70 °C, respectively.

5. Summary

Stability constants of the Nd(III) complex with nitrate were determined by spectrophotometry at elevated temperatures up to 70 °C, and the enthalpy of complexation was directly determined by microcalorimetry for the first time. Thermodynamic and spectroscopic data from this study suggest that the weak Nd(III) complex with nitrate has significant inner-sphere character and that the complexation is enhanced at elevated temperatures. The data help to evaluate the speciation of lanthanide(III) in nitrate solutions at elevated temperatures.

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