Laser-Induced Luminescence Study of Samarium(III) Thiodiglycolate Complexes

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The number and the geometric distribution of solvent molecules around a metal ion in solution are an important factor in the structural and chemical behavior of cation.[1-8] Indeed, such information has been utilized to design novel ionophores and receptors.[9-14] However, there have been few studies of hydration structure for lanthanides. The fact that many f-element salts which have relatively large lattice energies are fairly soluble in water is a reflection of the strength of the interactions between the metal cations and water molecules. In turn, this strong hydration competes with complexation by ligand as the process of complexation involves the displacement of one or more water molecules by a ligand. The techniques for studying the size and/or structure of the hydration sphere can be classified as direct or indirect methods. The direct methods include X-ray and neutron diffraction, extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR) relaxation measurements, luminescence decay. The indirect methods involve compressibility, NMR exchange and adsorption spectroscopy measurements.[15] The luminescence of trivalent lanthanides has presently extensively attracted in a variety of complexes in solution with much attention. This includes the determination of the local structures in crystalline materials, glasses, and solutions. The luminescence intensity and lifetime of trivalent lanthanide (Ln) and actinide (An) ions has been used to gain information on the composition and structure of the first coordination sphere of these ions in solution in materials ranging from inorganic compounds to systems of biological interest.[16] The luminescence lifetime of Ln and An is related to N_{H2O} (the number of H_2O molecules in the primary coordination sphere of the metal ion) due to the energy transfer from the excited state of the metal ion to the O-H vibration of the coordinated water molecules. A correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the N_{H2O} of trivalent lanthanide (Ln) and actinide (An) ions has therefore been investigated to establish a method for determining the N_{H2O} from measurements of the luminescence lifetime.[17] The calibration relations were derived on the basis of the linear correlation of the luminescence decay constant k_{obs} *vs.* volume percentage of H_2O in D_2O-H_2O solutions and the inner-sphere hydration number N_{H2O} in H_2O.[18-20]

Many efforts have been devoted to develop trivalent actinide/lanthanide separation using solvent extraction, ion exchange, and other techniques.[21,22] Efficient separation of trivalent Ans from Lns has been an important and rather difficult subject in the fields of inorganic chemistry and nuclear technology, because the two f-element series have similar range of ionic radii and show strong similarities in chemical behavior.

In this work we report a study of the luminescence lifetimes of Sm(III) in H_2O media when it is complexed to thiodiglycolate ligand which have S donor atoms. Variation of solution pH and of the samarium-ligand ratio were used to study both 1 : 1 and 1 : 2 complexation. Our goal was to use this technique to characterize the bonding properties of the sulfur donors to lanthanide ions.

Experimental Section

The Sm(III) stock solution (0.1 M) were prepared by dissolving precisely measured amount of Sm_2O_3 (Wako Pure Chem. Ind., Ltd.) in perchloric acid. The stock thiodiglycolic acid (TDA) solution was also prepared by dissolution of precisely measured amount of TDA (Kanto, Co., 97%) in doubly deionized H_2O. Sample solutions with various L/M ratio (L: total ligand concentration; M: Sm(III) ion concentration) were prepared by mixing an appropriate amount Sm(III) and ligand stock solution and diluted by 0.1 M $NaClO_4$ to final volume. Variation of the solution pH was effected by addition of small amount of NaOH or HCl directly to the quartz tube. The pH values were measured with an digital pH meter (Horiba) equipped with glass electrode. This pH meter was calibrated using three buffers (pH = 4, 7 and 9). The Sm(III) in the samples were excited to the excited states of Sm ($^6P_{3/2}$, 401 nm) by a pulsed laser beam. Subsequently, the emission from the lowest luminescent level to the ground state manifold, *i.e.*, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (594 nm) for Sm(III) was measured to obtain the luminescence lifetime.[23-26]

The 390-410 nm laser beam was obtained from a pulsed (10 Hz) 308 nm output of a Lambda Physik COMPex201 XeCl excimer laser pumping PBBO (Lambda Physik) in dioxane solution in a Lambda Physik SCANmate2 dye laser head. The pulse power was typically 3-7 mJ per pulse and the pulse width was about 15 nanoseconds. The focused output beam was directly to a quartz tube containing the solution of investigation. The emission light was collected at 90° into a Oriel 77257 monochromator using an optical fiber and detected by a Hamamatsu R928 photomultiplier tube. The whole emission wavelength range (12.8 nm width) was observed. The signal was fed into a Hewlett Packard 54510A digitizing oscilloscope which was connected to a personal computer through a GP-IB interface.

The luminescence lifetime measurements were carried out with the use of the detection system. Experiments were conducted at room temperature. A single exponential relation could analyze all luminescence decay curves observed in this work. The decay constants were calculated with a computer program using the regression procedure.

Results and Discussion

The hydration number of Sm(III) has been obtained by using the difference in the decay rate constants in H_2O and D_2O solutions.[27] In general, $k_{obs}(H_2O) >> k_{obs}(D_2O)$, $k_{obs}(D_2O) \approx$ constant, and ligands are not as effective in causing non-radiative de-excitation of the excited state. For Sm(III), a relationship has been proposed in which the hydration number is related directly to the decay rate constant in H_2O.[19] If there is no contribution from the ligand to the de-excitation of the luminescence excited state, the hydration of Sm(III) in the different complexes can be obtained directly from the values of k_{obs} measured in H_2O.

As shown in Figure 1, the k_{obs} of Sm(III) increased linearly with increasing the volume percentage of H_2O in the solutions, indicating that the quenching behavior of Sm(III) is mainly due to energy transfer from the excited states to OH vibrations of the hydrated H_2O. The lifetime τ of Sm(III) observed in H_2O and D_2O, *i.e.*, τ_{H_2O} = 2.7 ms and τ_{D2O} = 64 μs. The N_{H2O} of Sm(III) in H_2O were evaluated to be 9.0 ± 0.5 from measurements of the k_{obs} in H_2O and in samarium bromate, $[Sm(H_2O)_9](BrO_3)_3$, which has no ligand and nine water molecules in the first coordination sphere.[20]

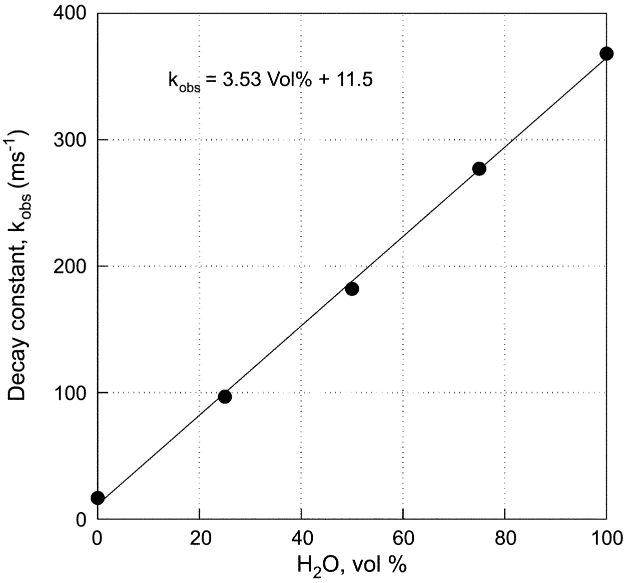

Figure 1. Luminescence decay constants k_{obs} for Sm^{3+} as a function of volume percentage of H_2O in D_2O-H_2O solutions.

Table 1. Stability Constants

Metal ion	Equilibrium	Log of Equilibrium Constant (at 25°C, I = 1.0)
H^+	HL/H.L	4.01
	H_2L/HL.H	3.11
Sm^{3+}	SmL/Sm.L	2.9
	SmL_2/Sm.L^2	4.68
	SmHL/Sm.HL	1.60
	$SmHL_2$/SmL_2.H	3.1

From the N_{H2O} in H_2O and the linear correlation obtained in D_2O-H_2O solutions, the following correlation was proposed for the determination of the hydration numbers of Sm(III).

$$N_{H_2O} = 2.54 \times 10^{-5}\, k_{obs}(H_2O) - 0.37 \qquad (1)$$

The uncertainty in the hydration numbers estimated by this method was reported to be ±0.5.

Relative fractions of the Sm, SmL, SmL_2, SmHL and $SmHL_2$ species were calculated as a function of the variation of pH and Sm-TDA ligand ratio by using the ligand protonation and complexation stability constants given in Table 1.[28]

This procedure allowed us to choose the optimum experimental conditions of metalligand ratio and pH to measure the luminescence lifetime of each species. The calculated fraction of the Sm, SmL, SmL_2, SmHL and $SmHL_2$ species formed in the solution are shown in Figure 2.

Experimental datas were also obtained by varying pH and [Sm]/[TDA] ratio in aqueous solution. Average number of water molecules coordinated to Sm(III) was determined by measuring excited-state lifetimes in H_2O solutions. The decay constants, k_{obs}(=1/lifetime), were used to calculated the average water molecules. The k_{obs} value of Sm(III) in aqueous solution increases linearly as the number of water molecules in the inner coordination sphere increase.

On the basis of lifetime results, the denticity of the ligands in the SmL and SmL_2 complexes have been calculated and are listed in Table 2. The hydration numbers obtained for the Sm(III)-TDA system is in poor accord with the expectation of tridentate ligand unit behavior by TDA. This ligand seems

Table 2. Calculated hydration number of Sm(III)-thiodiglycolate complexes

Sm Complexes	Hydration number
Sm	9.08
SmL	6.85
SmL_2	4.75
SmHL	6.55
$SmHL_2$	6.65

N_{H2O}(Sm-SmL) = 2.23, N_{H2O}(SmL-SmL_2) = 2.1

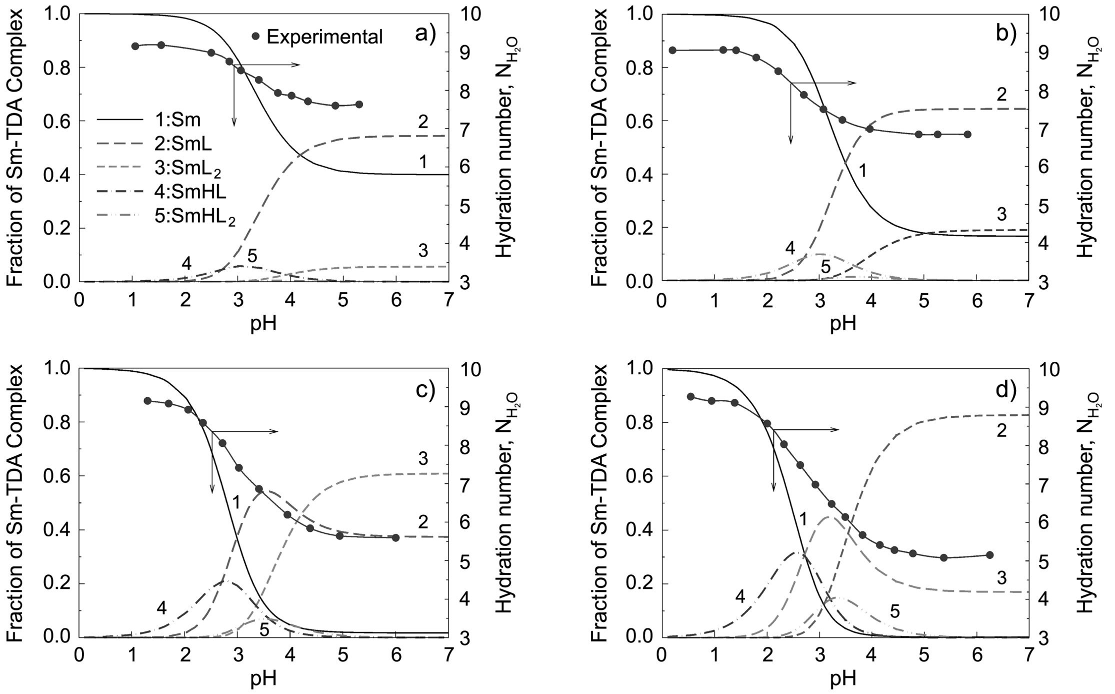

Figure 2. Distribution Sm(III)-thiodiglycolate and hydration number, N_{H2O} as a function of pH at $[Sm^{3+}] = 1 \times 10^{-3}$ and I = 0.1 M $NaClO_4$, for metal to ligand ratios: a) 1 : 1, b) 1 : 2, c) 1 : 7 and d) 1 : 18.

to displace approximately two coordinated water molecules in the Sm/TDA complexes. Thus the TDA ligand containing a central S neutral donor is shown to be poor chelator for free Sm(III) ion. This result indicates that the TDA ligand containing a soft sulfur donor does not bind to the hard acid lanthanide ions.

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