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Luminescence study on determination of the inner-sphere hydration number of Am(III) and Nd(III)

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Abstract

A correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the inner-sphere hydration number N_{H_2O} of Am(III) and Nd(III) in aqueous solution was investigated to establish a method for determining the N_{H_2O} from measurements of the luminescence lifetime. The calibration relations were proposed on the basis of the linear correlation of the k_{obs} vs. volume percentage of H_2O in D_2O–H_2O solutions and the N_{H_2O} in H_2O, i.e. nine for Am(III) and Nd(III). The k_{obs} of Am(III) and Nd(III) complexed with a series of polyaminopolycarboxylate ligands in H_2O and D_2O were measured to validate the calibration relations, and the N_{H_2O} and coordination numbers of these ions in the complexes were evaluated and compared with the other luminescent ions systematically. © 1998 Elsevier Science S.A.

Keywords: Americium(III); Neodymium(III); Luminescence lifetime; Inner-sphere hydration number; Polyaminopolycarboxylate complexes

1. Introduction

An inner-sphere hydration number N_{H_2O}, i.e. the number of H_2O molecules in the first hydration sphere, of a metal ion provides significant information regarding the coordination environment of the chemical species in solution, in solid and at their interface. The hydration of lanthanide ions in aqueous solution has been investigated by means of various methods: X-ray and neutron diffraction, extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR), etc. [1]. These investigations have been performed for aqueous solutions of high lanthanide concentrations of mol dm^{-3} (M) or above, whereas a luminescence method makes it possible to determine the N_{H_2O} in very dilute solutions, ca. mM or below of the metal concentrations, and is the most promising method for the hydration study of radioactive actinide ions. A correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the N_{H_2O} of trivalent actinide (Cm^{3+}) [2,3] and lanthanide (Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}) [4,5] ions has therefore been investigated to establish a method for determining the N_{H_2O} from measurements of the luminescence lifetime.

Americium(III) is the 5f analog of Eu(III) of which the luminescence has been studied extensively, the luminescence study of Am(III) has nevertheless been published much less than that of Cm(III) [6,7]. The luminescence from Am^{3+} in aqueous solution was first reported by Beitz et al. [8] although it has been known in nonaqueous solution ($POCl_3$) [9]. Subsequently, Yusov [10] reported luminescence lifetimes for Am^{3+} in D_2O and several protiated and deuterated organic solvents and a limit for the lifetime of Am^{3+} in H_2O. Some recent luminescence studies of trivalent f-element ions in solution have been reviewed with the experimental data on luminescence from aquated Am^{3+} in the context of prior f-element studies [11]. Recently, the luminescence spectra of Nd^{3+} complexes were observed for the first time in organic solvents [12], while the luminescence lifetimes of Nd^{3+} in H_2O and D_2O were found only in a review [13] as unpublished results [14]. Comparative study on the chemical properties of Am(III) and Nd(III) in solution is a significant and attractive subject in the coordination and separation chemistry of actinide and lanthanide elements in solution, since these ions have very similar ionic radii and spectral properties. However, the correlation between the k_{obs} and the N_{H_2O} is not known for Am(III) and Nd(III).

In the present study, the luminescence lifetimes of Am(III) and Nd(III) in D_2O–H_2O solutions have been measured to establish the calibration relations of k_{obs} vs. N_{H_2O} for these ions. The calibration relations obtained

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were applied to study the hydration states of Am(III) and Nd(III) complexes with polyaminopolycarboxylate ligands in aqueous solution.

2. Experimental

Am(III) stock solution was prepared from $^{241}AmO_2$ supplied by Amersham, UK. The concentration of the Am(III) solution (0.01 M $HClO_4$) was determined by α-ray spectrometry and liquid scintillation counting. Nd(III) stock solution in 0.01 M $HClO_4$ was prepared by dissolving an appropriate amount of Nd_2O_3 (Wako Pure Chem. Ind.) in perchloric acid. D_2O (99.9 at%) was obtained from Merck, Canada and used to prepare the D_2O–H_2O solutions and the complexes in D_2O. Nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetic acid (HEDTA), ethylenediamine-N,N′-diacetic-N,N′-dipropionic acid (ENDADP), ethylenediaminetetraacetic acid (EDTA), 1,2-diaminopropane-N,N,N′,N′-tetraacetic acid (PDTA), trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), glycoletherdiaminetetraacetic acid (EGTA) and triethylenetetraamine-N,N,N′,N″,N‴,N‴-hexaacetic acid (TTHA) were used as received from Tokyo Kasei Kogyo Co.. Solutions of the polyaminopolycarboxylate complexes were prepared by mixing stoichiometric amounts of metal(III) and ligand stock solutions of known concentration. The solution pH was adjusted by the addition of standard NaOH(D) or $H(D)ClO_4$ and was checked before and after the measurement of the luminescence lifetime. The concentration of Am(III) and Nd(III) in the samples was fixed in 1.2×10^{-5} and 1.0×10^{-2} M, respectively. The lifetimes of Am(III) and Nd(III) samples were measured using a 5-mm I.D. quartz cell and a standard 1-cm fluorimetry cell, respectively.

The metal(III) ion in the samples was excited to the excited states of Am ($^5L_6$, 504 nm) [15] and Nd ($^4G_{5/2}$,$^2G_{7/2}$, 593 nm) [16] by a pulsed laser beam. Subsequently, the emission from the lowest luminescent level to the groundstate manifold, i.e. $^5D_1\rightarrow{}^7F_1$ (691 nm) [17] for Am(III) and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (890 nm) [18] for Nd(III), was measured to obtain the luminescence lifetime. The 504 and 593 nm laser beam was obtained with a pulsed (10 Hz) 308 nm output of a Lambda Physik COMPex201 XeCl excimer laser pumping Coumarin 307 and Rhodamine 6G (Lambda Physik), respectively, in methanol 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 emission light was collected at 90° into an Oriel 77257 monochromator using an optical fiber and detected by a Hamamatsu R3896 photomultiplier tube. The whole emission wavelength range (12.8 nm width) was observed. Sharp cut optical filters (R series, Toshiba Glass Co.) were used to minimize the scattering laser light. The signal was fed into a Hewlett-Packard 54510A digitizing oscilloscope which was connected to a NEC PC-9801RX computer through a GP-IB interface. The luminescence decay curves observed in this work were fitted to single-exponential curves with correlation coefficients 0.99–0.999.

3. Results and discussion

The luminescence decay constants k_{obs} (s^{-1}) of Am^{3+} and Nd^{3+} were measured in D_2O–H_2O solutions as a function of volume percentage of H_2O. As shown in Fig. 1, the k_{obs} of these ions increased linearly with increasing the volume percentage of H_2O in the solutions with correlation coefficients above 0.999 for Am^{3+} and 0.99 for Nd^{3+}, indicating that the quenching behavior of the ions is due mainly to energy transfer from the excited states to OH vibrations of the hydrated H_2O, similar to Cm^{3+}, Eu^{3+}, etc.. The lifetimes τ of the ions observed in H_2O and D_2O, i.e. $\tau_{H_2O}=24.6\pm0.6$ ns and $\tau_{D_2O}=162\pm4$ ns for Am^{3+}, 32.4 ± 0.8 ns and 170 ± 4 ns for Nd^{3+}, are of the same order of magnitude, since the energy gaps of Am^{3+} (4942 cm^{-1}) and Nd^{3+} (5473 cm^{-1}), defined as the difference in energy between the emitting state and the next lower lying state, are similar to each other [17,18]. The lifetimes are summarized in Table 1 with the data in the literature. Our data of Am^{3+} and Nd^{3+} in H_2O and D_2O are very close to those of Beitz [11,14]. In the

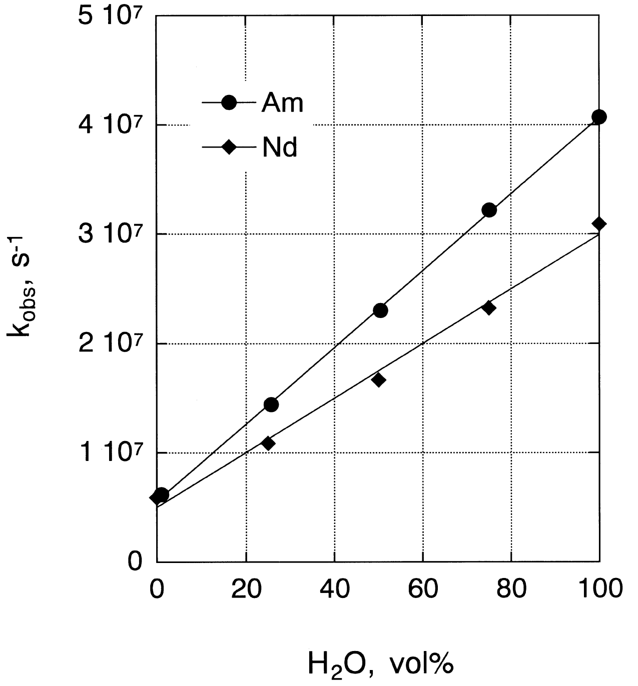

Fig. 1. Luminescence decay constants k_{obs} for Am^{3+} and Nd^{3+} as a function of volume percentage of H_2O in D_2O–H_2O solutions: $[Am^{3+}]=1.2\times10^{-5}$ M; $[Nd^{3+}]=1\times10^{-2}$ M.

Table 1
Luminescence lifetimes of Am^{3+} and Nd^{3+} in H_2O and D_2O

Am^{3+}			Nd^{3+}		
H_2O (ns)	D_2O (ns)	Ref.	H_2O (ns)	D_2O (ns)	Ref.
24.6 ± 0.6^a	162 ± 4^a	Present work	32.4 ± 0.8^b	170 ± 4^b	Present work
22 ± 3^c	155 ± 4^d	[11]	30	170	[13]
30 ± 6	200 ± 40	[19]			
<40	200 ± 50	[10]			

[a] Observed at $^5D_1\rightarrow{}^7F_1$.
[b] Observed at $^4F_{3/2}\rightarrow{}^4I_{9/2}$.
[c] Mean value ($^5D_1\rightarrow{}^7F_{0,1,2}$).
[d] Mean value ($^5D_1\rightarrow{}^7F_{1,2}$).

previous papers [2,4], the N_{H_2O} values of Cm^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} in H_2O were evaluated to be 9.2±0.5, 9.0±0.5, 9.1±0.5, 8.3±0.4 and 8.4±0.4, respectively, from measurements of the luminescence lifetime. In a spectral study of Nd^{3+} in fluid and frozen aqueous solutions, Rajnak and Couture [20] concluded that aquated Nd^{3+} in the first coordination sphere consists of nine water molecules. From the similarity of Am^{3+} spectra in $AmCl_3$, Am^{3+}:$LaCl_3$, and aquated Am^{3+} in fluid and frozen aqueous solutions, Carnall [21] concluded that aquated Am^{3+} has nine inner-sphere water molecules. The N_{H_2O} values of nine for Am^{3+} and Nd^{3+} in H_2O were therefore employed for the derivation of the calibration relations of k_{obs} (s^{-1}) vs. N_{H_2O}. From the linear correlation obtained in D_2O–H_2O solutions and the N_{H_2O} in H_2O, the following correlations were proposed for determination of the hydration numbers of these ions:

$$N_{H_2O} = 2.56\times10^{-7}k_{obs}(\mathrm{Am}) - 1.43, \tag{1}$$

$$N_{H_2O} = 3.58\times10^{-7}k_{obs}(\mathrm{Nd}) - 1.97. \tag{2}$$

Horrocks and Sudnick [22] have reported that the N_{H_2O} of Eu(III) and Tb(III) can be determined from the measurement of luminescence lifetimes separately in H_2O and D_2O solutions. If there is no contribution from the ligand to the deexcitation of the excited state, the N_{H_2O} of a metal ion in the different complexes can be obtained from the k_{obs} measured in H_2O. For Sm(III), Eu(III), Tb(III) and Dy(III), the correlations in which the N_{H_2O} is related directly to the k_{obs} in H_2O have been proposed by the same procedure described above and the validity of the correlations was confirmed in the hydration study of their polyaminopolycarboxylate complexes in aqueous solution [5]. Consequently, the hydration states of Am(III)– and Nd(III)–polyaminopolycarboxylate complex systems were studied in order to validate the applicability of Eqs. (1) and (2).

The k_{obs} values of Am(III) and Nd(III) complexed with NTA, EDTA, DTPA and TTHA in D_2O were measured at pH 4.0–5.0 and the N_{H_2O} were evaluated to be 0±0.4 for both ions in the complexes, indicating that these ligands were not effective in causing nonradiative deexcitation of the excited states for these ions. The quenching effect of CH vibration on the excited Am^{3+} was estimated using Eq. (1) from the lifetime data of Am^{3+} in $(CH_3)_2SO$ and $(CD_3)_2SO$ [10]. The difference of the effect in both solvents is equivalent to 0.25 H_2O molecules although the calculated N_{H_2O} are negative values in the solvents, indicating that the quenching by $(CH_3)_2SO$ is much less than that by D_2O. This also supports the fact that high-frequency ligand vibrations such as CH and CN give a slight contribution, however, the OH vibration of residual H_2O molecules in the complex is the primary quencher for the excited states of Am(III) and Nd(III).

The pH dependence of the hydration of Am(III) and Nd(III) in the presence of these ligands in H_2O was studied over the pH range of 1–11, as shown in Fig. 2(a,b). The hydration behavior of the complexes is similar qualitatively to the pH dependence of the hydration of Cm(III), Sm(III), Eu(III), Tb(III) and Dy(III) complexes in our previous papers [2,5] and of Eu(III) and Tb(III) complexes in the literature [23–25]. The coordination environment of the metal ion varies successively with pH, that is, free hydrated ions at lower pH, 1:1 complexes in the pH range of 4–8, and ternary hydroxo complexes at higher pH (ca. 9–11). In the case of the NTA system, the first plateau around pH 3–5 is caused by the formation of the $M(NTA)^0$ complexes and the second plateau at higher pH is due to the formation of the $M(NTA)_2^{3-}$ and $M(OH)_2^+$ complexes, according to the speciation calculation. The complexation of Am(III) with CDTA was not sufficient and that with ENDADP was shifted to the higher pH, compared with those of Nd(III). Average numbers of coordinated water molecules N_{H_2O}, ligand coordination numbers CN_L, and total coordination numbers CN_T of the 1:1 metal–polyaminopolycarboxylate complexes are summarized in Table 2. The CN_T were calculated as the sum of the CN_L and the N_{H_2O} measured, where $CN_L(NTA)=4$, $CN_L(HEDTA)=5.5$, $CN_L(ENDADP)=CN_L(EDTA)=CN_L(PDTA)=CN_L(CDTA)=6$, $CN_L(DTPA)=7.5$, $CN_L(EGTA)=8$ and $CN_L(TTHA)=8.5$ were employed as the number of the ligand donor groups [26]. The N_{H_2O} of Am(III) and Nd(III) in these complexes were apparently larger than those of Eu(III) and Tb(III) [5,24]. For the lanthanide(III)–polyaminopolycarboxylate complexes, the re-

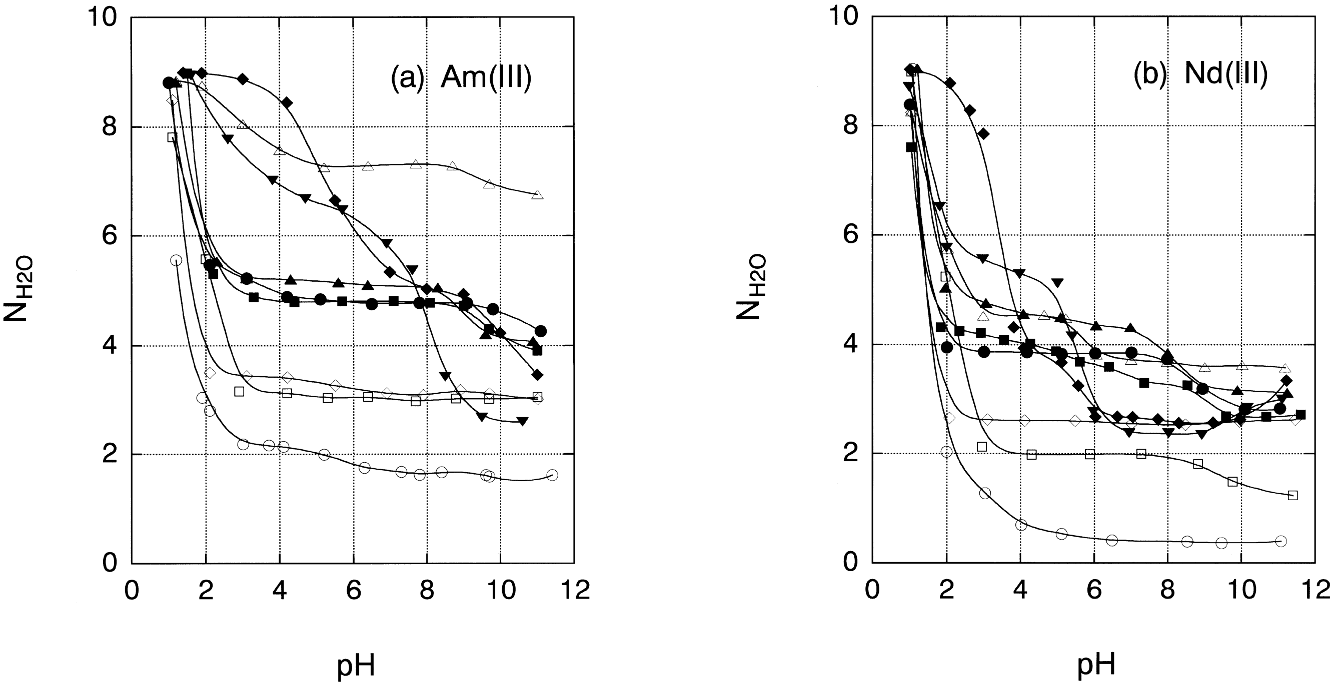

Fig. 2. Inner-sphere hydration numbers N_{H_2O} for (a) Am(III) and (b) Nd(III) in polyaminopolycarboxylate complexes as a function of pH: ○, TTHA; □, EGTA; ◇, DTPA; △, CDTA; ●, PDTA; ■, EDTA; ♦, ENDADP; ▲, HEDTA and ▼, NTA; [ligand]=[Am(III)]=1.2×10^{-5} M; [ligand]=[Nd(III)]=1×10^{-2} M.

sult $CN_T(Nd)=9.9$ is consistent with $CN_T(Sm)=10.2$, $CN_T(Eu)=8.9$, $CN_T(Tb)=8.6$ and $CN_T(Dy)=9.1$ [5] within the uncertainty of 0.4 H_2O molecules, indicating that the CN_T is about ten for the light lanthanides(III) and around nine for the heavy lanthanides(III) and that the change of the CN_T occurs between Sm(III) and Eu(III). In order to compare the CN_T of Am(III) and Cm(III), the N_{H_2O} values of Cm(III) in the complexes [2] were reevaluated using the calibration relation, $N_{H_2O}=6.12\times10^{-4}k_{obs}(Cm)-0.48$, obtained by the same procedure in this paper. This calibration relation is almost in agreement with that in the literature [2] and gives the same N_{H_2O} within 0.3 H_2O molecules. The recalculated N_{H_2O} values of the Cm(III) complexes were $N_{H_2O}(NTA)=6.3$, $N_{H_2O}(HEDTA)=4.3$, $N_{H_2O}(EDTA)=3.9$, $N_{H_2O}(CDTA)=3.9$, $N_{H_2O}(DTPA)=1.9$ and $N_{H_2O}(TTHA)=0.9$. The result $CN_T(Am)=10.7$ is appreciably larger than $CN_T(Cm)=9.8$ evaluated in a similar manner as above, suggesting that the CN_T of the actinide(III) complexes may be in the range between ten and eleven.

Table 2
Average numbers of coordinated water molecules N_{H_2O}, ligand coordination numbers CN_L, and total coordination numbers CN_T for Am(III)– and Nd(III)–polyaminopolycarboxylate complexes

Ligand	CN_L	Am(III)		Nd(III)	
		N_{H_2O} [a]	CN_T [b]	N_{H_2O} [a]	CN_T [b]
NTA	4	6.5	10.5	5.6	9.6
HEDTA	5–6	5.1	10.6	4.5	10.0
ENDADP	6	4.9	10.9	3.9	9.9
EDTA	6	4.8	10.8	4.0	10.0
PDTA	6	4.8	10.8	3.9	9.9
CDTA	6	7.3	13.3 [c]	4.5	10.5
DTPA	7–8	3.1	10.6	2.6	10.1
EGTA	8	3.0	11.0	2.0	10.0
TTHA	8–9	1.6	10.1	0.7	9.2
Average CN_T			10.7		9.9

[a] The uncertainty in the N_{H_2O} is about ±0.2–0.4.
[b] $CN_T=CN_L+N_{H_2O}$.
[c] This value was omitted for the calculation of the average CN_T.

In conclusion, our results suggest that the calibration relations proposed as Eqs. (1) and (2) for Am(III) and Nd(III) are valid to determine N_{H_2O} by measurements of the luminescence lifetime, and that the total coordination numbers of Am(III), Cm(III), Nd(III) and Sm(III) are possibly unity or above larger than those of Eu(III), Tb(III) and Dy(III) in the polyaminopolycarboxylate complexes.

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