Journal of Alloys and Compounds 275–277 (1998) 806–810

Luminescence study on hydration states of lanthanide(III)–polyaminopolycarboxylate complexes in aqueous solution

Takaumi Kimura*, Yoshiharu Kato

Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11, Japan

Abstract

The hydration states of lanthanide (Ln)(III) complexes (Ln=Sm, Eu, Tb and Dy) with a series of polyaminopolycarboxylate ligands were evaluated in detail on the basis of the linear correlation between the luminescence decay constants k_{obs} and the inner-sphere hydration number N_{H_2O} in D_2O–H_2O solutions. The k_{obs} of Ln(III) complexes in D_2O showed that these ligands were not effective in causing non-radiative de-excitation of the excited states for these ions. The N_{H_2O} of Sm(III) in a certain polyaminopolycarboxylate complex was apparently larger than those of Eu(III), Tb(III) and Dy(III) in the complexes. These results suggest that the empirical formulae proposed in this study are valid for the calibration of k_{obs} vs. N_{H_2O} and that the total coordination number, i.e. the sum of the number of ligand donor groups and the N_{H_2O} of Sm(III) is possibly unity larger than those of Eu(III), Tb(III) and Dy(III) in the complexes. © 1998 Elsevier Science S.A.

Keywords: Lanthanide(III) ions; Luminescence lifetime; Inner-sphere hydration number; Coordination number; Polyaminopolycarboxylate complexes

1. Introduction

Since the first use of polyaminopolycarboxylates in separation chemistry, lanthanide polyaminopolycarboxylate complexes have been a major research area in lanthanide coordination chemistry. In the past half century, many efforts have been devoted to determine the thermodynamic quantities of the complexes in aqueous solution [1–3]. However, the structure and composition of the coordination spheres of these complexes should be further clarified to understand the anomalous behavior of the so-called S-shape or gadolinium break in the thermodynamic parameters.

On the other hand, 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 at an atomic level. A correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the N_{H_2O} of trivalent lanthanide (Ln) and actinide (An) ions [4,5] has been investigated in D_2O–H_2O mixture solutions, in crystalline lanthanum compounds and in polyaminopolycarboxylate complexes to establish a method for determining the N_{H_2O} from measurements of the luminescence lifetime. In the previous paper [4], Ln(III) complexes with the polyaminopolycarboxylate ligands were employed for the calibration of k_{obs} vs. N_{H_2O}, because these ligands of which have the number and variety of arrangements of the donor groups form stable complexes with Ln(III) and the residual N_{H_2O} in the complexes are known for the Eu(III) and Tb(III) complexes [6]. In the course of the derivation of the calibration relations, it was assumed that for a given ligand the residual hydration of the Sm(III) and Dy(III) complexes is similar with that of the Eu(III) and Tb(III) complexes. However, the assumption should be reinvestigated carefully, since the thermodynamic parameters [2] and the N_{H_2O} [6] vary in the middle of the lanthanide series.

In this paper, the luminescence lifetimes of Ln(III) ions (Ln=Sm, Eu, Tb and Dy) have been measured with higher accuracy with respect to time than that in the previous work [4], to improve the calibration relations of k_{obs} vs. N_{H_2O} for these ions. The calibration relations were derived on the basis of the linear correlation of the luminescence decay constants k_{obs} vs. volume percentage of H_2O in D_2O–H_2O solutions and the inner-sphere hydration number N_{H_2O} in H_2O. To validate the calibration relations, the hydration states of Ln(III) complexed with a series of polyaminopolycarboxylate ligands were measured in detail by varying [ligand]/[metal] ratio and pH, and the coordi-

---

*Corresponding author.

PII: S0925-8388(98)00446-0

nation numbers of the Ln(III) ions in the complexes were evaluated systematically.

2. Experimental

Ln(III) stock solutions were prepared by dissolving an appropriate amount of Ln_2O_3 (Wako Pure Chem. Ind., Ltd.) 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 Ln(III) 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., Ltd. Solutions of the polyaminopolycarboxylate complexes were prepared by mixing stoichiometric amounts of Ln(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 during the measurement of the luminescence lifetime. The concentration of Ln(III) in the samples was fixed in 1×10^{-2} M.

The Ln(III) in the samples was excited to the excited states of Sm ($^6P_{3/2}$, 401 nm) [7], Eu ($^5L_6$, 394 nm) [8], Tb ($^5D_2$, 355 nm) [9] and Dy ($^4I_{11/2}$, 355 nm) [7] by a pulsed laser beam. Subsequently, the emission from the lowest luminescent level to the groundstate manifold, i.e. $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (594 nm) for Sm(III), $^5D_0\rightarrow{}^7F_2$ (615 nm) for Eu(III), $^5D_4\rightarrow{}^7F_5$ (543 nm) for Tb(III), $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (479 nm) for Dy(III), was measured to obtain the luminescence lifetime. The 355-nm (third harmonic) laser beam was obtained directly with a pulsed (10 Hz) output of a Spectron SL-803 Nd:YAG laser. The 390–410 nm laser beam was obtained with 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 ns. The emission light was collected at 90° into an 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 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 Ln^{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 Ln^{3+} increased linearly with increasing the volume percentage of H_2O in the solutions with correlation coefficient above 0.999, indicating that the quenching behavior of Ln^{3+} is due mainly to energy transfer from the excited states to OH vibrations of the hydrated H_2O. The lifetimes τ of Ln^{3+} observed in H_2O and D_2O, i.e. $\tau_{H_2O}=2.7$ μs and $\tau_{D_2O}=64$ μs for Sm^{3+}, 110 and 3700 μs for Eu^{3+}, 450 and 4100 μs for Tb^{3+}, 2.5 and 43 μs for Dy^{3+}, decreased with decreasing an energy gap, in the order of Tb^{3+} (14 804 cm^{-1})$>Eu^{3+}$(12 255 cm^{-1})$>Sm^{3+}$(7438 cm^{-1})$>Dy^{3+}$(7374 cm^{-1}), defined as the difference in energy between the emitting state and the next lower lying state [10,11]. The N_{H_2O} of Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} in H_2O were evaluated to be 9.0±0.5, 9.1±0.5, 8.3±0.4 and 8.4±0.4 [4], respectively, from measurements of the k_{obs} in H_2O and in lanthanide bromate, $[Ln(H_2O)_9](BrO_3)_3$, which has no ligand and nine water molecules in the first coordination sphere. Considering information from X-ray and neutron diffraction, fluorescence, Raman and visible spectroscopy, etc., Rizkalla and Choppin [6] concluded that the light lanthanides (La^{3+}–Nd^{3+}) form a series with the hydration number of 9, whereas the heavier elements (Tb^{3+}–Lu^{3+}) apparently form octahydrates. The middle-series lanthanides (Nd^{3+}–Tb^{3+}) either assume intermediate structures or a rapid exchange equilibrium exists

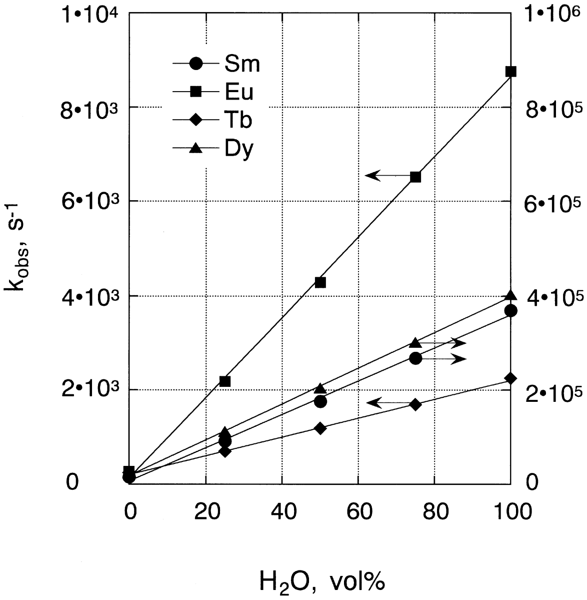

Fig. 1. Luminescence decay constants k_{obs} for Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} as a function of volume percentage of H_2O in D_2O–H_2O solutions: $[Ln^{3+}]=1\times10^{-2}$ M.

between both hydrate structures. The N_{H_2O} of 9 for Sm^{3+} and Eu^{3+} and of 8 for Tb^{3+} and Dy^{3+} in H_2O were employed for the derivation of the calibration relations of k_{obs} vs. N_{H_2O}, since the trend of our results were close to the conclusion of Rizkalla and Choppin [6]. From the N_{H_2O} in H_2O and the linear correlation obtained in D_2O–H_2O solutions, the following correlations were proposed for the determination of the hydration numbers of Ln(III).

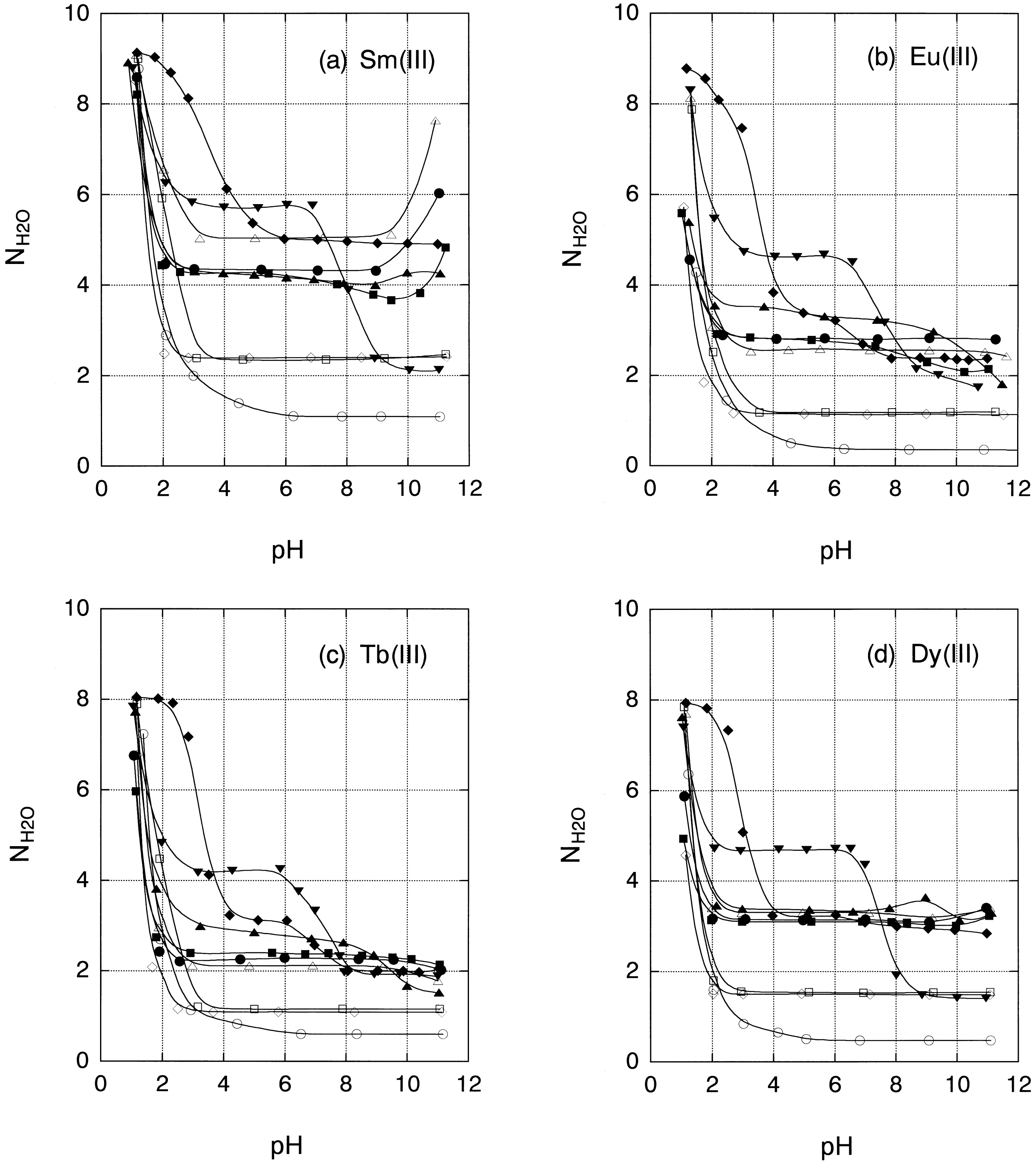

Fig. 2. Inner-sphere hydration numbers N_{H_2O} for (a) Sm(III), (b) Eu(III), (c) Tb(III) and (d) Dy(III) in polyaminopolycarboxylate complexes as a function of pH: (○) TTHA; (□) EGTA; (◇) DTPA; (△) CDTA; (●) PDTA; (■) EDTA; (♦) ENDADP; (▲) HEDTA; and (▼) NTA; $[ligand]=[Ln(III)]=1\times 10^{-2}$ M.

$$N_{H_2O} = 2.54 \times 10^{-5} k_{obs}(\mathrm{Sm}) - 0.37 \tag{1}$$

$$N_{H_2O} = 1.05 \times 10^{-3} k_{obs}(\mathrm{Eu}) - 0.44 \tag{2}$$

$$N_{H_2O} = 4.03 \times 10^{-3} k_{obs}(\mathrm{Tb}) - 0.87 \tag{3}$$

$$N_{H_2O} = 2.11 \times 10^{-5} k_{obs}(\mathrm{Dy}) - 0.60 \tag{4}$$

The N_{H_2O} of Eu(III) and Tb(III) has been obtained by using the difference in the k_{obs} in H_2O and D_2O solutions [12]. For Eu(III) and Cm(III), the relationship has been proposed in which the N_{H_2O} is related directly to the k_{obs} in H_2O [5,13] and utilized successfully to determine the N_{H_2O} of various species [14]. The slopes of Eq. (2) and Eq. (3) for Eu(III) and Tb(III), respectively, agreed with those in the literature [12] within ±5%. Eqs. (2) and (3) should give results consistent with those obtained by the procedure of Horrocks and Sudnick [12] within the uncertainty of the luminescence method, ±0.5 water molecules. This suggests that Eq. (2) and Eq. (3) are reliable for determination of the N_{H_2O} of Eu(III) and Tb(III) and, presumably, Eq. (1) and Eq. (4) for Sm(III) and Dy(III), respectively.

The residual hydration of the complexes for Eu(III) and Tb(III) has been determined by luminescence measurements [15–18]. By using the calibration relations (Eqs. (1)–(4)), the hydration states of Ln(III)–polyaminopolycarboxylate complex systems were studied in order to validate the applicability. The k_{obs} of Ln(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 as 0±0.3, indicating that these ligands were not effective in causing non-radiative de-excitation of the excited states for the Ln(III) ions.

The k_{obs} of the Ln(III) complexes were measured by varying [ligand]/[Ln(III)] ratio, *R*, in the range of $R = 1$–76 at pH 5.0±0.5. The N_{H_2O} for *R* were almost independent of *R* for Ln(III) complexed with TTHA, EGTA and DTPA, whereas those in the complexes with CDTA, PDTA, EDTA, ENDADP and HEDTA decreased with increasing *R*. The different trends of decrease of the N_{H_2O} were found between the complexes with CDTA, PDTA and ENDADP and with EDTA and HEDTA. In the former complexes, the N_{H_2O} was kept constant up to about $R = 10$ and ca. one to two H_2O molecules were further removed from the inner sphere of the 1:1 complex at $R = 76$. The N_{H_2O} of the latter complexes decreased gradually with increasing *R* and ca. two to three H_2O molecules were lost from the 1:1 complex at $R = 76$. These results suggest that Ln(III) forms the 1:2 complexes with the polyaminopolycarboxylate ligands in the higher *R* region, because the primary coordination sphere of Ln(III) cannot be covered by one molecule of the hexadentate ligand. In case of the Ln(III)–NTA complexes, ca. three to four H_2O molecules were further removed from the 1:1 complex by the formation of the 1:2 complex and the N_{H_2O} were constant at above $R = 2$.

The pH dependence of the hydration of Ln(III) in the presence of these ligands was studied over the pH range of 1–11, as shown in Fig. 2(a–d). The hydration behavior of the Ln(III) complexes is similar to the pH dependence of the hydration of the Eu(III) and Tb(III) complexes in the literature [15–17]. There are three buffer regions; the first at lower pH in which the N_{H_2O} of the cations is equivalent to that of free ions; a second in the pH range of 4–8 in which the N_{H_2O} is that of the metal ion in the 1:1 complex; and a third at higher pH (ca. 9–11) associated possibly with the formation of ternary hydroxo complexes. This pattern is not followed by the NTA system. The speciation calculation using stability constants [19] shows that a first plateau in pH 3.0–6.0 is caused by the formation of the $\mathrm{Ln(nta)}^0$ complexes and that a second plateau at pH 9.0–11.0 is due to the formation of the $\mathrm{Ln(nta)}_2^{3-}$ and $\mathrm{Ln(OH)}_2^{+}$ complexes. Table 1 summarized average numbers of coordinated water molecules N_{H_2O}, ligand coordination numbers CN_L, and total coordination numbers CN_T of the 1:1 Ln(III)–polyaminopolycarboxylate complexes.

Table 1
Average numbers of coordinated water molecules N_{H_2O}, ligand coordination numbers CN_L, and total coordination numbers CN_T for lanthanide(III)–polyaminopolycarboxylate complexes

Ligand	CN_L	Sm(III)		Eu(III)		Tb(III)		Dy(III)	
		N_{H_2O}	CN_T	N_{H_2O}	CN_T	N_{H_2O}	CN_T	N_{H_2O}	CN_T
NTA	4	5.8	9.8	4.7	8.7	4.2	8.2	4.7	8.7
HEDTA	5–6	4.2	9.7	3.4	8.9	2.9	8.4	3.4	8.9
ENDADP	6	5.0	11.0	3.3	9.3	3.0	9.0	3.2	9.2
EDTA	6	4.2	10.2	2.8	8.8	2.4	8.4	3.1	9.1
PDTA	6	4.3	10.3	2.8	8.8	2.3	8.3	3.1	9.1
CDTA	6	5.0	11.0	2.6	8.6	2.1	8.1	3.3	9.3
DTPA	7–8	2.4	9.9	1.1	8.6	1.1	8.6	1.5	9.0
EGTA	8	2.3	10.3	1.2	9.2	1.2	9.2	1.5	9.5
TTHA	8–9	1.1	9.6	0.4	8.9	0.6	9.1	0.5	9.0
av. CN_T			10.2		8.9		8.6		9.1

The uncertainty in the N_{H_2O} is about ±0.2–0.4. $CN_T = CN_L + N_{H_2O}$.

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 [18]. The N_{H_2O} in each 1:1 complex and the CN_T in the complexes, i.e. $CN_T(Eu)=8.8\pm0.5$ and $CN_T(Tb)=8.5\pm0.5$, of Eu(III) and Tb(III) agreed well with those in the literature [6]. As mentioned above, the energy gaps of Sm(III) and Dy(III) are quite similar to each other, which indicates a similar quenching behavior of the ions in aqueous solution. Nevertheless, the N_{H_2O} of Sm(III) were apparently larger than those of Dy(III) in the complexes.

In summary, our results suggest that the calibration relations proposed as Eqs. (1)–(4) are valid to determine the N_{H_2O} by measurement of the luminescence lifetime, and that the total coordination number of Sm(III) is possibly unity larger than those of Eu(III), Tb(III) and Dy(III) in the polyaminopolycarboxylate complexes.

References

[1] T. Moeller, D.F. Martin, L.C. Thompson, R. Ferrus, G.R. Feistel, W.J. Randall, Chem. Rev. 65 (1965) 1.
[2] R.M. Smith, A.E. Martell, Sci. Tot. Environ. 64 (1987) 125.
[3] G.R. Choppin, P.J. Wong, Lanthanide aminopolycarboxylates, in: G.B. Kauffman (Ed.), Coordination Chemistry, A Century of Progress, ACS Symposium Series 565, Am. Chem. Soc., Washington, DC, 1994.
[4] T. Kimura, Y. Kato, J. Alloys Compounds 225 (1995) 284.
[5] T. Kimura, G.R. Choppin, J. Alloys Compounds 213–214 (1994) 313.
[6] E.N. Rizkalla, G.R. Choppin, Hydration and hydrolysis of lanthanides, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on Physics and Chemistry of Rare Earths, vol. 15, Elsevier, Amsterdam, 1991.
[7] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4424.
[8] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4450.
[9] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4447.
[10] G. Stein, E. Würzberg, J. Chem. Phys. 62 (1975) 208.
[11] J.V. Beitz, Similarities and differences in trivalent lanthanide- and actinide-ion solution absorption spectra and luminescence studies, in: K.A. Gschneidner Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on Physics and Chemistry of Rare Earths, vol. 18, Elsevier, Amsterdam, 1994.
[12] W.D. Horrocks Jr., D.R. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.
[13] P.P. Barthelemy, G.R. Choppin, Inorg. Chem. 28 (1989) 3354.
[14] T. Kimura, G.R. Choppin, Y. Kato, Z. Yoshida, Radiochim. Acta 72 (1996) 61.
[15] H.G. Brittain, J.P. Jasinski, J. Coord. Chem. 18 (1988) 279.
[16] H.G. Brittain, G.R. Choppin, P.P. Barthelemy, J. Coord. Chem. 26 (1992) 143.
[17] C.A. Chang, H.G. Brittain, J. Telser, M.F. Tweedle, Inorg. Chem. 29 (1990) 4468.
[18] G.R. Choppin, J. Alloys Compounds 192 (1993) 256.
[19] A.E. Martell, R.M. Smith, Critical Stability Constants, Plenum Press, New York, 1974.