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Luminescence study on the inner-sphere hydration number of lanthanide(III) ions in concentrated aqueous salt solutions in fluid and frozen states[1]

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Abstract

Luminescence lifetimes of lanthanide[Ln](III) ions [Ln=Sm, Eu, Tb and Dy] in concentrated aqueous solutions at room and at liquid nitrogen temperatures were measured by means of time-resolved laser-induced luminescence spectroscopy. The inner-sphere hydration number N_{H_2O} of Ln(III) was estimated on the basis of the correlation between the N_{H_2O} and the lifetime obtained in D_2O–H_2O solutions at each temperature. In fluid states of sodium chloride, nitrate and perchlorate solutions at room temperature, the N_{H_2O} of the Ln(III) ions indicate that nitrate ion forms inner-sphere complex with these ions, whereas chloride and perchlorate ions do not, and that the concentrated perchlorate ion would perturb the hydration structure of Ln(III). In frozen states of the solutions at liquid nitrogen temperature, the formation of the inner-sphere chloro and nitrate complexes of Ln(III) is suggested in chloride and nitrate solutions, respectively, but not in perchlorate solution. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

In recent years, the hydration of lanthanide(III) ions in aqueous solutions has been investigated by means of various methods: X-ray [1–5] and neutron [6–9] diffraction, extended X-ray absorption fine structure (EXAFS) [10], Raman spectroscopy [11–13], luminescence spectroscopy [14–17], and so on. Although the results obtained with the different methods are not necessarily consistent with each other, a majority of the data supports that the hydration number of the lanthanide(III) ions changes from nine for the light ions (La^{3+}–Nd^{3+}) to eight for the heavy ions (Tb^{3+}–Lu^{3+}) with a decrease from nine to eight for the intermediate ions (Nd^{3+}–Tb^{3+}) [18]. The above-mentioned investigations, except the luminescence spectroscopy, have been carried out for aqueous solutions of high lanthanide(III)-salt concentrations of mol dm^{-3}(=M) or above, while the luminescence method makes it possible to determine the inner-sphere hydration number N_{H_2O} of a

metal ion in very dilute solutions, ca. mM or below of the metal concentrations. As an extension of the method reported by Horrocks and Sudnick [19] for Eu(III) and Tb(III), we have investigated a correlation between the luminescence decay constant k_{obs} (the reciprocal of the excited state lifetime) and the N_{H_2O} of trivalent lanthanide (Nd, Sm, Eu, Tb and Dy) [20,21] and actinide (Am and Cm) [22–24] ions to establish a method for determinining the N_{H_2O} from the measurement of the luminescence lifetime. The luminescence lifetimes of Eu(III) chloride [15–17], nitrate [14–17], perchlorate [14,16,17], sulfate [16] and thiocyanate [15] solutions have been so far measured in fluid states at room temperature, and the inner- and/or outer-sphere complexation of Eu(III) with the inorganic ligands has been discussed from the variation of the luminescence lifetimes and/or the spectra. However, little has been studied for the other lanthanides in fluid and frozen solutions by the luminescence measurements. Since the thermodynamic parameters [25,26] and N_{H_2O} [18] vary in the middle of the lanthanide series, comparison of the N_{H_2O} among the lanthanide ions is interesting from the viewpoint of the coordination structure and bonding of the ions in various aqueous solutions.

In the present study, the luminescence lifetimes of the

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lanthanide[Ln](III) ions [Ln=Sm, Eu, Tb and Dy] in sodium chloride, nitrate and perchlorate solutions in both fluid and frozen states were measured by means of time-resolved laser-induced luminescence spectroscopy. The estimated N_{H_2O} were compared with results from X-ray and neutron scattering experiments, from EXASF data and from Raman spectra in the literature.

2. Experimental

Ln(III) stock solutions in 0.01 M $HClO_4$ were prepared by dissolving an appropriate amount of 99.9% Ln_2O_3 (Wako Pure Chem. Ind., Ltd.) in perchloric acid. Salt solutions were prepared from doubly distilled deionized water containing various concentrations, i.e., 0.1 M to near saturation, of NaCl, $NaNO_3$ or $NaClO_4$. The concentration of Ln(III) in the samples was fixed in 0.01 M at pH around two. D_2O (99.9 at.%) was obtained from Merck, Canada and used to prepare the D_2O–H_2O solutions and the salt solutions in D_2O. The lifetimes of fluid samples at room temperature were measured using a standard 1-cm fluorimetry cell. Frozen samples were prepared by immersing the aqueous solutions in a 4-mm-I.D. quartz cell into liquid nitrogen quickly, a cooling rate about 600–800 $K\ min^{-1}$, just before the luminescence measurements, and were maintained in a special quartz Dewar vessel at liquid nitrogen temperature during the measurements.

The Ln(III) in the samples was excited to the excited states of Sm^{3+} ($^6P_{3/2}$, 401 nm), Eu^{3+} ($^5L_6$, 394 nm), Tb^{3+} ($^5D_2$, 355 nm) and Dy^{3+} ($^4I_{11/2}$, 355 nm) by a pulsed laser beam [21]. 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), $^5D_0 \rightarrow {}^7F_1$ (592 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 from a pulsed (10 Hz) output of a Spectron SL-803 Nd:YAG laser. 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 ns. The emission light was collected at 90° into a Oriel 77257 monochromator using a optical fiber and detected by a Hamamatsu R928 photomultiplier tube. The whole emission wavelength range (12.8 nm width) was observed. Sharp cut optical filters (Y or O 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 co-efficients of 0.99–0.999.

3. Results and discussion

The hydration number of Eu(III) and Tb(III) has been obtained by using the difference in the decay rate constants in H_2O and D_2O solutions [19]. From the linear relations of k_{obs} versus volume percentage of H_2O in D_2O–H_2O solutions and the N_{H_2O} of Ln^{3+} in H_2O, i.e., nine for Sm^{3+} and Eu^{3+} and eight for Tb^{3+} and Dy^{3+}, in fluid states, the calibration relations of k_{obs} versus N_{H_2O} were proposed for determining the N_{H_2O} of Ln(III) from the measurements of the luminescence lifetimes [21]. These correlations were applied to study the hydration states of Ln(III)-polyamino-polycarboxylate complexes in aqueous solution and the validity of the correlations was confirmed within the uncertainty of ±0.4 H_2O molecules.

In D_2O–H_2O solutions in frozen states at liquid nitrogen temperature, the measured k_{obs} of the Ln^{3+} ions as shown in Fig. 1 increased linearly with increasing the volume percentage of H_2O in the solutions with correlation coefficient above 0.999 similarly in fluid states, indicating the quenching of the ions due to energy transfer from the excited states to OH vibrations of the hydrated H_2O even in frozen states. Couture and Rajnak [27] presented the evidence that similar 4f-state energy level structures exist for Er^{3+} in $ErCl_3 \cdot 6H_2O$ and hydrated Er^{3+} in fluid and frozen aqueous solutions. They concluded that hydrated Er^{3+} and hydrated Gd^{3+} have eight water molecules in the first coordination sphere. In a spectral study of Nd^{3+} in fluid and frozen aqueous solutions, Rajnak and Couture [28] concluded that the first coordination sphere of hydrated Nd^{3+} consists of nine water molecules. From the EXASF data in the concentrated aqueous Ln(III) perchlorate solutions at room and at liquid nitrogen tempera-
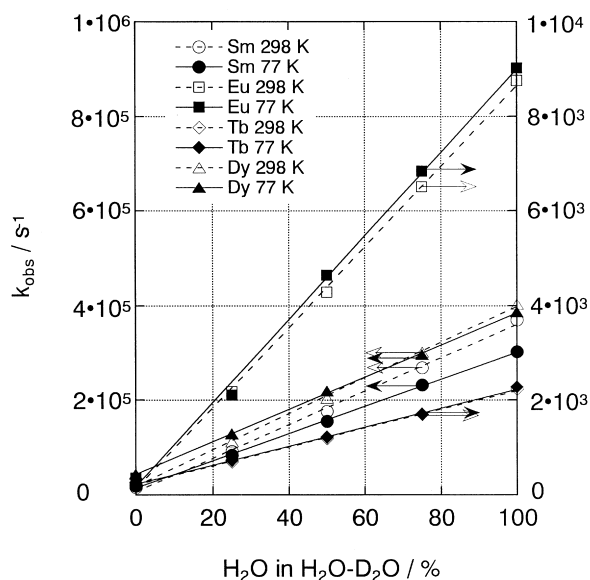

Fig. 1. Luminescence decay constants k_{obs} for Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} as a function of volume percentage of H_2O in D_2O–H_2O solutions at room and at liquid nitrogen temperatures: $[Ln^{3+}]$=0.01 M.

tures, Yamaguchi et al. [10] have reported that in both liquid and glassy states the N_{H_2O} is about nine for the light Ln^{3+} and around eight for the heavy Ln^{3+} and that the change of the N_{H_2O} occurs in the range of Sm^{3+} to Gd^{3+}. These suggest that the N_{H_2O} of Ln^{3+} in frozen solution are equal to those in fluid solution. For Ln(III) in aqueous solutions in frozen states, the derivation of the calibration relations of k_{obs} versus N_{H_2O} was therefore performed in a

similar manner as that in fluid states. The calibration relations for each Ln(III) in fluid and frozen states are shown in Fig. 1 and also Fig. 2, respectively, and are used to determine the N_{H_2O} in the salt solutions.

Fig. 2 shows the N_{H_2O} of Ln(III) as a function of salt concentration in fluid aqueous salt solutions at room temperature. The trends for the variation of the N_{H_2O} in each solution were similar among the Ln(III) ions and

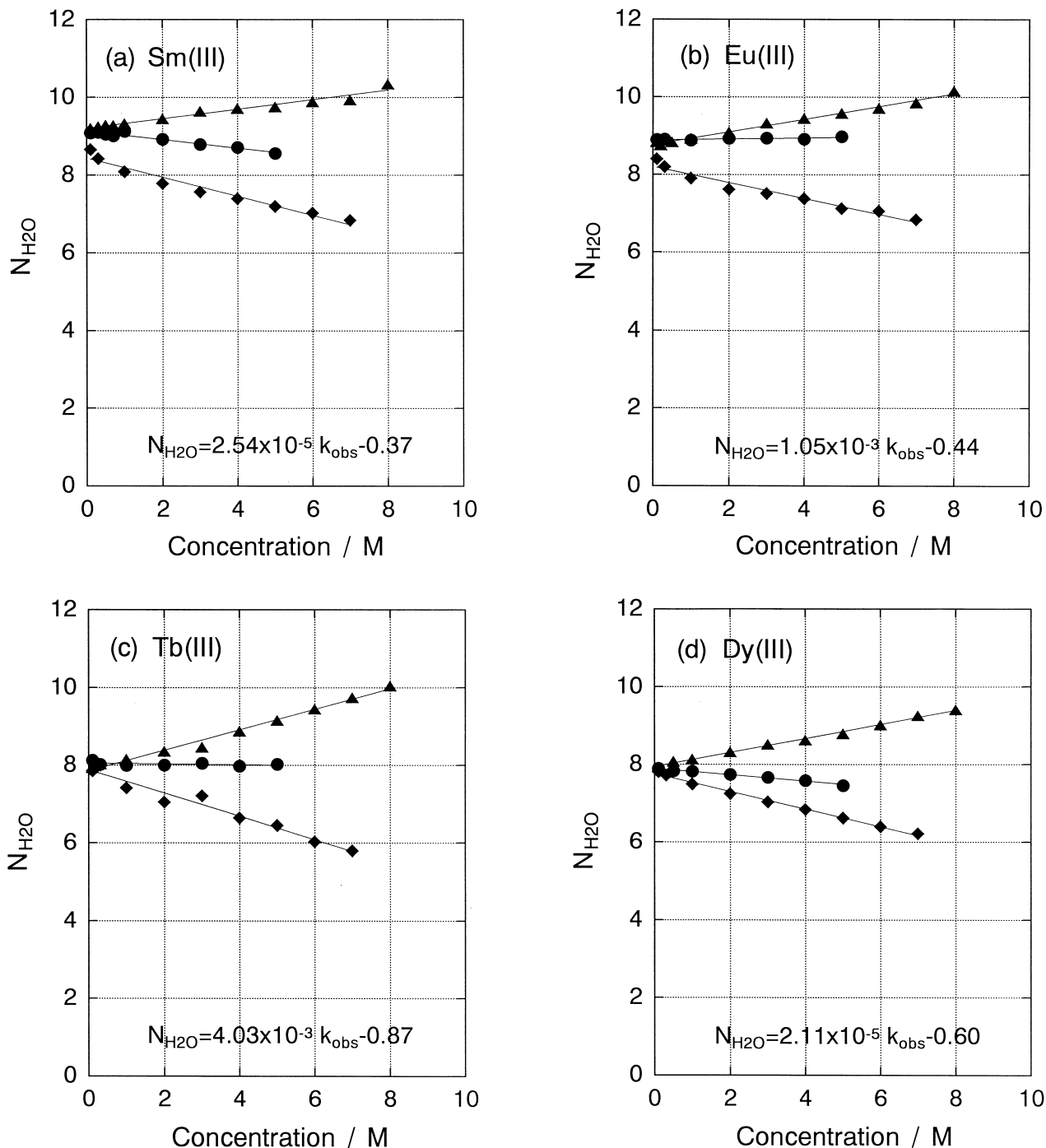Fig. 2. The inner-sphere hydration number N_{H_2O} of (a) Sm(III), (b) Eu(III), (c) Tb(III) and (d) Dy(III) as a function of salt concentration in fluid aqueous solutions at room temperature: [Ln(III)]=0.01 M; ●, NaCl; ♦, NaNO$_3$; ▲, NaClO$_4$.

could be approximated by linear relationships with correlation coefficient about 0.99 as shown in Fig. 2. The k_{obs} of Ln(III) in 0.1–5 M salt solutions in D_2O were also measured at room temperature and the N_{H_2O} in each solution in fluid states were evaluated to be 0±0.3 by using the calibration relations, indicating that the inorganic ligands were not effective in causing non-radiative de-excitation of the excited states for the Ln(III) ions and that the N_{H_2O} determined by measurements of the lifetime of Ln(III) in H_2O should give results consistent with those obtained by the procedure of Horrocks and Sudnick [19]. The N_{H_2O} in 0.1–5 M chloride solutions show a nearly constant value for Eu(III) and Tb(III) or a slight decrease for Sm(III) and Dy(III), ca. 0.5 H_2O molecule at 5 M NaCl. These results agree with the luminescence lifetime study of Eu(III) in the literature [16,17] and suggest the outer-sphere interaction between Ln(III) and chloride ion, although the luminescence excitation spectroscopy [15] exhibits the partial inner-sphere complexation of Eu(III) by the chloride ion. Our results are also in qualitative agreement with the results from X-ray [1–3,5] and neutron [6–8] scattering experiments of Ln(III). Furthermore, the shift in the hypersensitive absorption band ($^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$) of Nd(III) [29] and the NMR chemical shift of La-139 [30] vary from zero only above 5 M chloride concentration. This data supports the outer-sphere complexation of Ln(III) by the chloride ion in the concentration range below 5 M. In 0.1–7 M nitrate solutions, the N_{H_2O} of Ln(III) decreased with increasing the concentration of nitrate ion, indicating the inner-sphere complexation of Ln(III) by the nitrate ion, similar to results for Eu(III) in the literature [14–17]. Approximately two H_2O molecules were removed from the first coordination sphere of Ln(III) at 7 M NaNO3, suggesting the formation of $[M(NO_3)(H_2O)_n]^{2+}$ with the nitrate ion functioning as a bidentate ligand. The N_{H_2O} of Ln(III) in 0.1–8 M perchlorate solutions increased with increasing the concentration of perchlorate ion and similar results were observed in the luminescence study of Eu(III) [14–17] with the contradicting interpretations. From measurements up to 6 M total perchlorate concentration, Bünzli and Yersin [14] and Breen and Horrocks [15] indicate that Eu(III)-perchlorate interaction must have an exclusively outer-sphere nature. Tanaka and Yamashita [16] suggest an increase in the N_{H_2O} of Eu(III) as a decrease in the luminescence lifetime with an increase in the perchlorate concentration. However, it would seem more likely that this is due to a perturbation of the hydrate equilibria of Eu(III) caused by the outer-sphere complexation [15]. Furthermore, Lis and Choppin [17] proposed a model involving a relatively constant N_{H_2O} with the enhanced quenching due to stronger Ln^{3+}–OH_2 interaction as the secondary hydration of Ln(III) is reduced by the increased competition of the $Na^+(H^+)$ and ClO_4^- ions. The mechanism of the increased quenching of Ln(III) could not be elucidated explicitly by the luminescence study. Since the perchlorate ion cannot

quench these cations, the concentrated perchlorate ion would perturb the hydration structure of Ln(III). For the nearly constant N_{H_2O} of Ln(III) in the perchlorate concentration below 7–9 M, our conclusions are consistent with the results from the studies of X-ray [4,5] and neutron [8,9] diffraction, EXAFS [10] and the hypersensitive absorption band of Nd(III) [29] as no evidence for inner sphere complexation by the perchlorate ion below 7–9 M $HClO_4$ has been found by the various measurement systems.

Fig. 3 shows the N_{H_2O} of Ln(III) as a function of salt concentration in frozen aqueous salt solutions at liquid nitrogen temperature. The observed N_{H_2O} were almost independent of the salt concentration in each solution within the experimental conditions. Approximately one and 2–3 H_2O molecules were removed from the inner-sphere of Sm(III), Eu(III) and Tb(III) in chloride and nitrate solutions, respectively, suggesting the formation of the inner-sphere chloro and nitrate complexes. For Dy(III), ca. 1–2 H_2O molecules were further removed from the inner-sphere than those of the other Ln(III). The temperature dependency of the stability constants K for chloro and nitrate complexes were evaluated to compare the results shown in Fig. 2 and also Fig. 3. The stabilities of complexes are governed by both enthalpy and entropy changes according to

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{1}$$

where the changes in free energy, ΔG^0, are related to the stability constants by

$$-\Delta G^0 = RT \ln K \tag{2}$$

The enthalpy and entropy changes for formation of $LnCl^{2+}$ and $LnNO_3^{2+}$ (Ln = Sm, Eu, Gd, Tb and Dy) in 1 M $LiClO_4$ were obtained by solvent extraction method in temperature range of 0–50°C [31]. According to the calculation using Eq. (1) and Eq. (2), and ΔH^0 and ΔS^0 in the literature, all of the stability constants K for $LnCl^{2+}$ and $LnNO_3^{2+}$ complexes increases with decreasing temperature from 25–0°C, e.g., K = 1.19–1.94 for $EuCl^{2+}$ and K = 17.9–28.0 for $EuNO_3^{2+}$, respectively. This suggests that the chloride and nitrate complexation of Ln(III) would be promoted during cooling processes of the samples, and consequently the N_{H_2O} of Ln(III) in frozen states would be reduced much more than those in fluid states by temperature effects of the complexation, especially at lower concentrations of the salt solutions. Kanno and Hiraishi [11–13] have reported Raman studies of Ln(III) chlorides and nitrates at room and at liquid nitrogen (in the glassy state) temperatures and with variable ratios of water to salt. The Ln^{3+}–OH_2 stretching Raman band in the glassy nitrate solutions changed in frequency rather smoothly from La(III) to Lu(III) nitrate solution. For glassy solutions of $EuCl_3$ and $GdCl_3$ the Raman band was split into a doublet and the population of the higher hydrate species
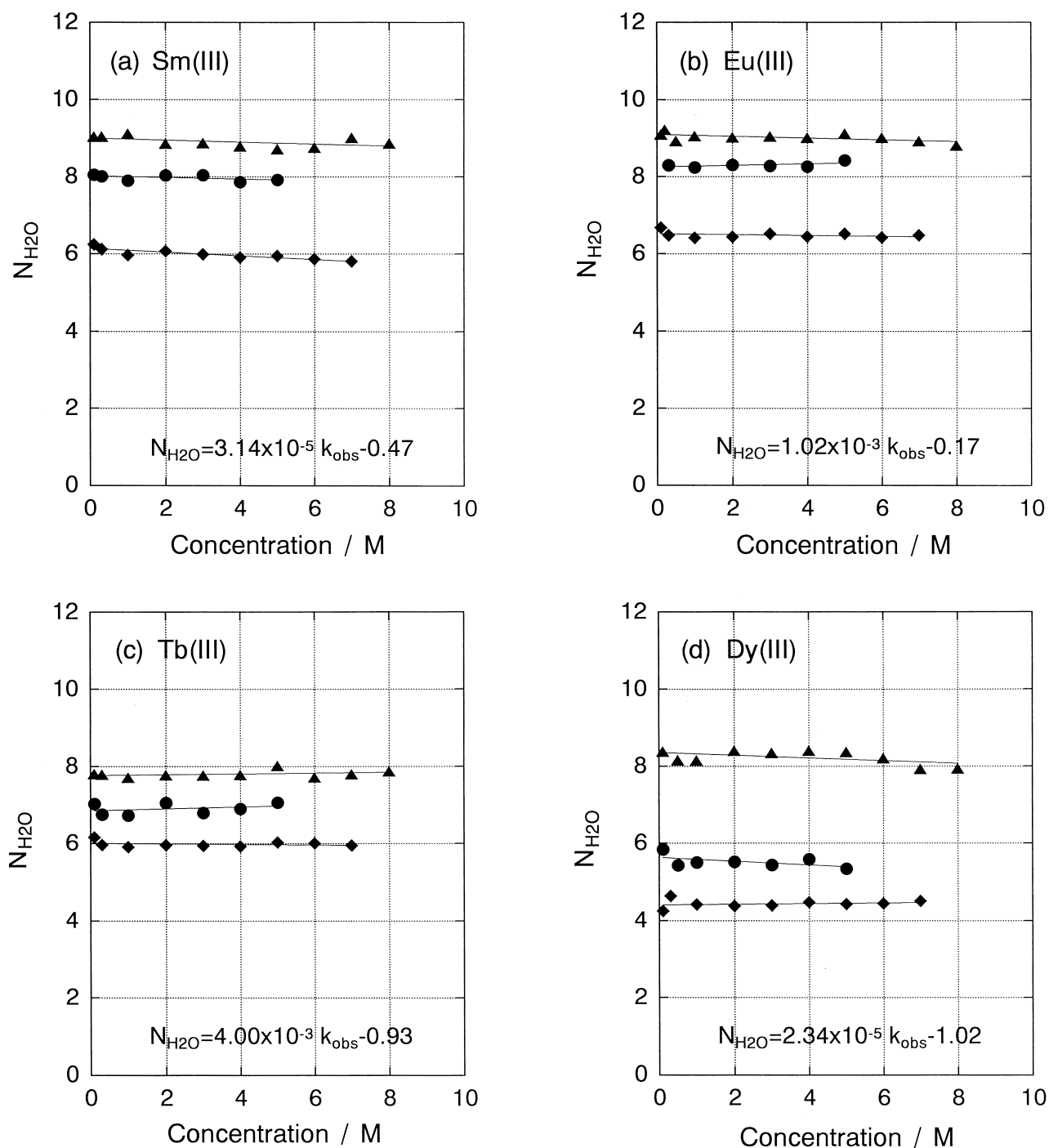
Fig. 3. The inner-sphere hydration number N_{H_2O} of (a) Sm(III), (b) Eu(III), (c) Tb(III) and (d) Dy(III) as a function of salt concentration in frozen aqueous solutions at liquid nitrogen temperature: [Ln(III)] = 0.01 M; ●, NaCl; ♦, NaNO$_3$; ▲, NaClO$_4$.

increased with increasing the salt concentration, so-called anomalous concentration dependence. However, this effect could not be observed in the N_{H_2O} of Eu(III) in frozen chloride solutions as shown in Fig. 3(b). The N_{H_2O} of Ln^{3+} in perchlorate solutions was equal to those in H$_2$O solution without the salt, i.e., ca. nine for Sm^{3+} and Eu^{3+} and ca. eight for Tb^{3+} and Dy^{3+}, indicating the inner-sphere complexes of Ln(III) were not formed in perchlorate

solutions. As mentioned above, EXAFS study [10] showed that the N_{H_2O} of Ln(III) in the concentrated aqueous Ln(III) perchlorate solutions in glassy state at liquid nitrogen temperature are equal to those in liquid state at room temperature. If these results are valid for the wide concentration range of the perchlorate ion, the N_{H_2O} of Ln(III) should be constant as presumed in fluid perchlorate solutions.

In summary, the quenching behavior of Ln(III) ions in frozen solution was similar to that in fluid solution owing to energy transfer from the excited states to OH vibrations of the hydrated H_2O. For Ln(III) in aqueous solutions in frozen states, the calibration relations of k_{obs} versus N_{H_2O} were therefore proposed in a similar manner as those in fluid states. The N_{H_2O} of Sm(III), Eu(III), Tb(III) and Dy(III) measured in aqueous salt solutions showed similar behavior with each other as a function of salt concentration in fluid and frozen states, respectively. The anomalous concentration dependence of the N_{H_2O} found in the Raman band of $EuCl_3$ and $GdCl_3$ solutions could not be observed in frozen chloride solutions. However, the hydration structure of Ln(III), especially in frozen solutions, should be further examined from the viewpoints of the salt concentration and temperature effects on the inner- and/or outer-sphere complexation with the inorganic ligands by means of various methods.

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