

A puzzle of Gd-break and tetrad effect of aqueous lanthanide(III)-EDTA complex formation: Different Racah parameters between two lanthanide-EDTA complex series with distinct hydration states

Iwao Kawabe*

Department of Earth and Planetary Sciences, Graduate School of Environmental Studies,
Building-E of Faculty of Science, Nagoya University
Chikusa, Nagoya 464-8602, Japan

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Corresponding e-mail address: kawabe@eps.nagoya-u.ac.jp

Abstract

The logarithmic formation constants ($\log K$) for aqueous lanthanide(III)-EDTA complexes show a Gd-break and subtle tetrad effect, but the ΔS_r and ΔH_r data indicate step-like changes in the middle Ln. UV-Vis spectra of Eu^{3+} for Eu-EDTA solution suggest the hydration change occurring across the middle Ln-EDTA series. This is supported by the recent studies of luminescence kinetics on the inner-sphere waters of Eu-EDTA and Tb-EDTA, and by the lanthanide-induced ^{17}O NMR shifts of Ln-EDTA. Such spectroscopic studies allow to re-examine the long-lasting controversy of the Gd-break and tetrad effect of $\log K(\text{Ln-EDTA})$. Here is proposed a thermodynamic model to elucidate it from the viewpoints: i) hydration changes of Ln-EDTA and light $\text{Ln}^{3+}_{(\text{aq})}$ series, ii) the nephelauxetic effect due to the coordination change of Ln^{3+} of Ln-EDTA, and iii) the improved equation of Jørgensen theory applicable to ΔH_r and ΔG_r . This model satisfies the spectroscopic constraints on the hydration states of Ln-EDTA series: Three and two water molecules exist in the inner spheres of light Ln(La~Nd)-EDTA and heavy Ln(Dy~Lu)-EDTA series, respectively. Each middle Ln(Sm~Tb)-EDTA is a mixture of the two hydrate species, and their abundances are given by the equilibrium of hydration change reaction: $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_3]_{(\text{aq})} = [\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$. The ΔH_r , ΔS_r and ΔG_r data for Ln-EDTA formation, when corrected for hydration changes in Ln-EDTA and light $\text{Ln}^{3+}_{(\text{aq})}$ series, can be fitted by the improved equation of Jørgensen theory, and the thermodynamic parameters for the formation of two Ln-EDTA series from octahydrate $\text{Ln}^{3+}_{(\text{aq})}$ have been evaluated. The hydration change of middle Ln-EDTA series explains the apparent Gd-break of

$\log K(\text{Ln-EDTA})$. The nephelauxetic effect by the change in coordination number for Ln^{3+} (ΔCN) is evident in ΔH values for the three reactions: (a) $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_3]^-$ (aq) formation from $\text{Ln}_{(\text{oct}, \text{aq})}^{3+}$ ($\Delta\text{CN}=+1$), (b) $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]^-$ (aq) formation from $\text{Ln}_{(\text{oct}, \text{aq})}^{3+}$ ($\Delta\text{CN}=0$), and (c) the hydration change reaction of Ln-EDTA given as (b)-(a) ($\Delta\text{CN}=-1$). The relative Racah E^1 parameter values for Nd^{3+} , $\Delta E^1(\text{Nd}^{3+})$, from the tetrad effects of ΔH for (a), (b) and (c), are $+(39 \pm 14) \text{ cm}^{-1}$, $-(19 \pm 7) \text{ cm}^{-1}$, and $-(58 \pm 18) \text{ cm}^{-1}$, respectively. The ΔH_r values for (a) with $\Delta\text{CN}=+1$ show a large convex tetrad effect, and the ΔS_r values also exhibit a similar tetrad effect. Therefore, their tetrad effects are significantly cancelled in ΔG_r . This is a reason why the subtle tetrad-like variation of $\log K(\text{Ln-EDTA})$ is asymmetrical between light and heavy Ln, along with the hydration change effects of middle Ln-EDTA and light $\text{Ln}_{(\text{aq})}^{3+}$ series cancelled partly within the light Ln.

Introduction

The logarithmic formation constants ($\log K$) for aqueous lanthanide(III)-chelate complexes are fairly different among chelate agents, and they show different patterns of series variations (Moeller et al., 1965; Geier and Karlen, 1971; Moeller, 1973; Choppin et al., 1977; Thompson, 1979; Suzuki, 1999). Some examples of $\log K$ for the typical (1:1) Ln(III) complexes with DTPA, EDTA, NTA, and dipicolinate are shown in Fig. 1. They are important references when we consider Ln(III)-complexation in natural solutions of geochemical interest (Wood, 1990; Millero, 1992; Hass et al., 1995; Byrne and Sholkovitz, 1996; Johannesson et al, 1996; Ohta and Kawabe, 2000a, b).

The average $\log K$ value tends to increase with the number of electron donor groups of the complexing agent in Fig. 1: DTPA, EDTA, NTA, and dipicolinate have the donor groups of 8, 6, 4, and 3, respectively. The positive entropy change in the complex formation by the release of water molecules from the inner coordination sphere of $\text{Ln}^{3+}_{(\text{aq})}$ gives the large positive ΔS_r values, which makes ΔG_r ($=-2.303RT\log K$) negative and contributes to the stabilization of aqueous Ln(III) complexes (Grenthe, 1964; Moeller, 1973 and Thompson, 1979). The series change pattern of $\log K$, on the other hand, is different from one complex series to another. Among the four examples of (1:1) complexes shown in Fig. 1, Ln-EDTA series appears somewhat distinct because its series change of $\log K$ indicates the Gd-break (Schwarzenbach and Gut, 1956) with a small tetrad-like variation (Fidelis and Siekierski, 1966), whereas those for the other three series do not exhibit such characteristics clearly. The Gd-break and tetrad-like variation of $\log K$ (Ln-EDTA) have a long history of debates as below.

Wheelwright et al. (1953) noted the Gd-break in the series change of $\log K(\text{Ln-EDTA})$ determined by themselves, and interpreted it as the change of hexadentate EDTA^{4-} to the pentadentate one in the heavy Ln series from their view of the "steric hindrance" in coordination structures of Ln(III)-carboxylate complexes. Schwarzenbach and Gut (1956), however, argued that the Gd-break of $\log K$ is observed in Ln-EDTA, Ln-CyDTA, or Ln-NTA series, and emphasized the importance of half-filled ($4f^7$) effect at Gd^{3+} . Eventually the former interpretation has been favored in subsequent studies (Moeller, 1973).

The tetrad-like variation of $\log K$ (Ln-EDTA) was first noted by Fidelis and Siekierski (1966) as an additional example of their "regularity" in the separation factors for successive Ln given by the ratio of the complex stability constants, $\beta = K_{(Z+1)}/K_{(Z)}$, for Ln(III)-phosphonic acid derivatives (HEH ϕ P and HDEHP) complexes. Rowlands (1967), however, argued that the proposal by Fidelis and Siekierski (1966) was based on insufficient data and left doubt as to the general validity, except for only the two complexes with HEH ϕ P and HDEHP. Peppard et al. (1969) put forth the lanthanide tetrad effect in the logarithmic partition coefficients ($\log D$) for Ln(III) in two solvent-extraction systems with a phosphinic acid derivative (H[DOP]) and a phosphonate (DEH[CIMP]). Peppard et al. (1970) showed that the regularity of $\beta = K_{(Z+1)}/K_{(Z)}$ in HEH ϕ P by Fidelis and Siekierski (1966) remarkably resembles the tetrad effect in $\log K$ for the system of Ln(III)-H[DOP]. Jørgensen (1970) and Nugent (1970) explained the experimental proposal of tetrad effect by Peppard et al. (1969) from Jørgensen's (1962) theory of the refined spin-pairing energy theory (RSPET).

Thompson (1979) noted Jørgensen's RSPET in a considerable length in his review on aqueous Ln(III) complexes, but it was cited in relation to the spectroscopic study, not to the thermodynamic one. Hence this might have provided such an impression that there were no close relation between thermodynamic properties of Ln(III)-complex formation and Jørgensen's RSPET. Kawabe and Masuda (2001) showed that the experimental tetrad effects by Peppard et al. (1969) can be described quantitatively by the improved equation of RSPET (Kawabe, 1992).

The interpretation of lanthanide tetrad effect may explain the Gd-break as the octad effect variation involved in the tetrad effect (Peppard et al., 1969; Nugent, 1970; Kawabe, 1992). The regularity of $\beta = K_{(Z+1)}/K_{(Z)}$ by Fidelis and Siekierski (1966), which is now called the double-double effect in logK by their group (Mioduski and Siekierski, 1975; Fidelis and Mioduski, 1981), is the same as the tetrad effect by Pappard et al. (1969). Recently Kawabe (2013a) re-evaluated the acceptable logK(Ln-EDTA) values and their uncertainties: When suitable corrections to the standardized condition of 25°C and $\mu=0.1$ (KCl or KNO₃) are made for the logK(Ln-EDTA) values by different methods and followed by normalization with logK(Y-EDTA), they converge within 2 σ (mean) errors less than 0.9 % for all Ln. Kawabe (2013a) have confirmed that the Gd-break with small tetrad-like variations certainly exists beyond the experimental errors, but he also noted that the tetrad-like variations is not so symmetrical as Jørgensen's RSPET predicts, which may be a distinct feature possibly affected by the hydration changes across Ln(III)EDTA(aq) and Ln³⁺(aq) series.

In Fig. 1, most of (1:1) Ln(III)-chelate complexes except Ln-EDTA do not appear to

show the Gd-break with tetrad effect very clearly. This situation is mostly interpreted as the circumstantial evidence against the importance of Gd-break and tetrad effect. This may be a reason why the majority of solution chemists and geochemists tend to be skeptical about the Gd-break and tetrad effect. Nevertheless, we have reported a considerable number of REE studies directly showing evidence for the tetrad effect and Jørgensen's theory (Kawabe, 1992; Kawabe, 1999a, b; Ohta and Kawabe, 2000a, b and 2001; Kawabe and Masuda, 2001; Tanaka and Kawabe, 2004; Miura et al., 2004).

Recently, Kawabe (2013b) showed that the data of ΔG_r , ΔH_r and ΔS_r for Ln-DTPA complex formation can be regressed by the improve RSPET equation successfully, when they are corrected for the hydration changes of light $\text{Ln}^{3+}(\text{aq})$ series. The smoothly curved trend of $\log K$ for Ln-DTPA series (Fig. 1) is resulting from the similar convex tetrad effects of ΔH_r and $T\Delta S_r$ cancelled significantly in ΔG_r ($= -2.303RT\log K$). Hence, the apparently smooth variation of $\log K(\text{Ln-DTPA})$ cannot be the immediate evidence against the importance of tetrad effects and Jørgensen's theory (RSPET). The purpose of this study is to re-examine the experimental data of ΔG_r , ΔH_r and ΔS_r for aqueous Ln(III)-EDTA complex formation from the same viewpoints as those of Ln-DTPA formation (Kawabe, 2013b). The specific objectives will be set forth after providing a brief summary of key previous works on the hydration change of Ln-EDTA series in the next.

Brief summary of key previous works and the objectives of present study

Geier and Karlen (1971), on the basis of the thermodynamic data for Ln-EDTA

complex formation, revealed that the hydration states are different between the light and heavy Ln-EDTA series, and that middle Ln-EDTA is a mixture of two distinguishable species belonging to the respective isomorphous Ln-EDTA series. Ots (1973a) endorsed it from the enthalpy and heat capacity changes for the formation of Ln-EDTA complexes from MgEDTA^{2-} at 10, 20, 30, and 40°C in 1.0 M NaClO_4 medium: the series change of ΔC_p at 25°C exhibits a maximum peak for Ln=Eu. The peak corresponds to the condition that two Eu-EDTA species with distinct hydration states coexist with approximately equal abundances (Ots, 1973b).

Geier et al. (1969) showed that the (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$) absorption band of Eu^{3+} for Eu(III)-EDTA solution is composed of two peaks at 395 and 394 nm, and that the peak ratio varies considerably with temperature from 2 to 81 °C. Geier and Jørgensen (1971) also reported that the (${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$) absorption band of Eu(III)-EDTA solution at 580 nm are splitting into two peaks separated by 14 cm^{-1} , and that the intensity ratio of two peaks changes monotonously with increasing temperature from 25 to 80°C. The absorption between the levels with J=0 precludes the splitting due to the ligand-field effect. Therefore, this is a spectroscopic line of evidence that the aqueous Eu-EDTA complex is a mixture of two distinct Eu-EDTA species with different hydration states (Thompson, 1979). Graepi et al. (1995) re-determined the splitting of (${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$) absorption band of Eu^{3+} for Eu(III)-EDTA solution and the other Eu(III)-polyaminocarboxylate complexes as a function of temperature and pressure. They evaluated the ΔH_r , ΔS_r , and ΔV_r values for the hydration change reaction between the two species of Eu(III)-EDTA complex. Their ΔH_r and ΔS_r values are almost the

same as those by Geier et al. (1969) from the (${}^7F_0 \rightarrow {}^5L_6$) absorption data.

The luminescence decay constants for Eu(III)-EDTA and Tb(III)-EDTA in normal and heavy water media (Horrocks and Sudnick, 1979), showed that the numbers of water molecules in the first-coordination spheres (q_w) are 3.5 ± 0.5 for Eu-EDTA and 2.8 ± 0.5 for Tb-EDTA. However, Bryden and Reilly (1982) reported that $q_w = 2.5$ for Eu-EDTA. Rizkalla and Choppin (1991) and Brittain et al. (1992) also gave $q_w = 2.6 \pm 0.5$ for both Eu-EDTA and Tb-EDTA. Kimura and Kato (1998) applied the luminescence method not only to the complexes of Eu(III) and Tb(III) but also to those of Sm(III) and Dy(III), in which $q_w = 4.2 \pm 0.3$ for Sm-EDTA, 2.8 ± 0.3 for Eu-EDTA, 2.4 ± 0.3 for Tb-EDTA, and 3.1 ± 0.3 for Dy-EDTA. Beeby et al. (1999) re-considered the importance of oscillators other than OH of bound water molecules in the non-radiative deexcitation process for aqueous Ln(III) complexes, and they concluded that $q_w = 2.6 \pm 0.3$ (Eu-EDTA) and $q_w = 2.9 \pm 0.3$ (Tb-EDTA). In response to Beeby et al. (1999), Supkowski and Horrocks (2002) revised the original equation for q_w of Eu complexes given by Horrocks and Sudnick (1979) into the following form that $q_w = A(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1} - \alpha)$ with $A = 1.11$ (water molecules \cdot ms) and $\alpha = 0.31$ (ms^{-1}), and then they re-calculated that $q_w(\text{Eu-EDTA}) = 2.7 \pm 0.1$. This became compatible with $q_w(\text{Eu-EDTA}) = 2.5$ (Bryden and Reilly, 1982), 2.6 ± 0.5 by Rizkalla and Choppin (1991) and Brittain et al. (1992), 2.8 ± 0.3 (Kimura and Kato, 1998) and 2.6 ± 0.3 (Beeby et al., 1999). The five values of $q_w(\text{Eu-EDTA})$ by the luminescence method give $q_w = 2.64 \pm 0.10$ ($n=5$) as the mean and two SD for the mean. Hence it is certain that the Eu-EDTA complex involves water molecules of $q_w = 2.6$ in the inner coordination sphere.

In view of the lanthanide-induced shifts (LIS) in nuclear resonances, ^{13}C , ^{23}Na , ^2H , ^{17}O , and ^{35}Cl NMR studies of aqueous Ln(III) complexes including those with EDTA have been reported (Sherry et al., 1980; Bryden et al. 1981). Alpoim et al.(1992) showed that the hydration numbers of Dy(III)-polyaminocarboxylate complexes can be determined from Dy(III)-induced water ^{17}O shifts because of the dominant contribution of the contact term in the observed shifts. They demonstrated that the number of inner-sphere water molecules in various aqueous Dy(III) complexes estimated from water ^{17}O shifts are comparable with those evaluated from the studies by luminescence decay constants, in which $q_w(\text{Dy-EDTA})=2.3$ was reported. Caravan et al. (1997) extended the viewpoint by Alpoim et al.(1992), and re-interpreted the lanthanide-induced ^{17}O shifts of D_2O for aqueous Ln-EDTA complexes reported by Bryden et al. (1981). They concluded that the light Ln-EDTA series (Ln=Pr, Nd, and Eu) and heavy Ln-EDTA series (Ln=Tb~Yb) involve the inner-sphere water molecules of 2.5 and 2.0, respectively. This supports the spectroscopic and thermochemical arguments for the hydration changes in middle Ln-EDTA series.

The hydration state of Ln-EDTA series and its change across the series have been fairly well documented in the UV-Vis, luminescence kinetics, and ^{17}O MNR studies as well as thermochemical ones for last thirty years. Nevertheless, the previous studies did not explain why the series change of $\log K(\text{Ln-EDTA})$ is exhibiting a Gd-break with a small tetrad-like variation unlike those for the other (1:1) Ln(III) complexes (Fig. 1). Hence the main objective of this study is to give a quantitative answer to the long-standing problem. In addition, we will make sure the following two points: 1) the hydration change of Ln-EDTA series is analogous to the hydration change of light

Ln³⁺(aq) series (Rizkalla and Choppin, 1991; Kawabe, 1999a; Kawabe et al., 2006a, b and references therein), therefore the overall effects of hydration changes in Ln³⁺(aq) and Ln-EDTA series on logK for the formation of Ln-EDTA complexes are partly cancelled in light Ln, unlike other cases, and 2) the hydration change of Ln-EDTA complex series also immediately suggests that Racah parameters of Ln³⁺ are different between the two Ln-EDTA series because of the nephelauxetic effect correlating with the interatomic distance between Ln³⁺ and ligand (Reisfeld and Jørgensen, 1977; Tröster, T., 2003; Kawabe et al., 2006b). The decrease of coordination number for Ln(III) reduces the average distance between Ln³⁺ and ligands in the complex. This makes the covalency of bonding between Ln³⁺ and ligand greater, and then Racah parameters for Ln³⁺ in the Ln(III) complexes must be reduced. However, little attention has been paid to this point in the previous studies except Geier et al. (1969).

Results and Discussion

1) Experimental data of ΔH_r , ΔS_r , and ΔG_r for Ln(III)-EDTA formation

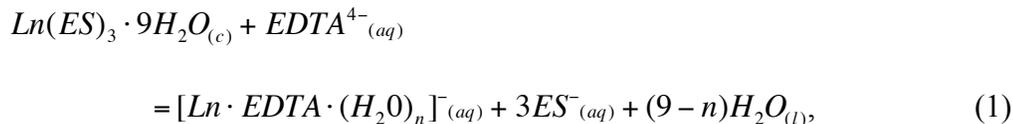
Mackey et al. (1962) reported their ΔH_r data for the formation of aqueous Ln(III)-EDTA complexes at 25°C and an ionic strength $\mu=0.1$. They calculated $\Delta S_r [= (\Delta H_r - \Delta G_r)/T]$ using $\Delta G_r (= -2.303RT \log K)$ reported by Betts and Dahlinger (1959). Table 1 lists the values of ΔH_r , ΔS_r and ΔG_r accepted by Mackey et al. (1962). According to Mackey et al. (1962), a relative uncertainty of their ΔH_r data (one sigma S. D.) is less than 0.2 (kJ/mol), and those of ΔG_r are ranging from 0.04 - 0.15 (kJ/mol). Therefore, a relative uncertainty for ΔS_r is less than 2 (J/mol/K).

Geier and Karlen (1971) discussed the hydration change of Ln-EDTA series using the polarographic data of $\Delta G_r (= -2.303RT \log K)$ by Schwarzenbach et al. (1954) and ΔH_r data by Mackey et al. (1962). Kawabe (2013a), as noted as above, showed that the reported five data sets of $\log K(\text{Ln-EDTA})$ by potentiometry with glass electrode (Wheelwright et al., 1953) and Pb- and Cu-ion selective electrodes (Suzuki et al., 1980), polarography (Schwarzenbach et al., 1954), and the radiotracer-cation exchange (Betts and Dahlinger, 1959), converge well within $2\sigma(\text{mean})$ less than 0.9 %, when appropriate corrections for the standardized condition and the subsequent normalization to $\log K(\text{Y-EDTA})=17.62$ are made for them. Table 1 lists the values of $\Delta G_r = -2.303 \log K$ by Kawabe (2013a), together with the calculated ΔS_r values using the ΔH_r data by Mackey et al. (1962). The differences in ΔG_r between Betts and Dahlinger (1959) and Kawabe (2013a) are fairly small, so that the ΔS_r values of the two sets in Table 1 are approximately the same within experimental errors.

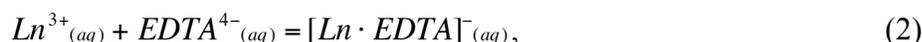
2) Hydration changes of Ln(III)-EDTA and light $\text{Ln}^{3+}_{(\text{aq})}$ series

Before going to the discussion of Gd-break and tetrad-like series variation of $\log K(\text{Ln-EDTA})$, we will make sure the nature of hydration change of Ln(III)-EDTA series on the basis of the accepted thermodynamic data of Mackey et al. (1962) listed in Table 1. The hydration change of Ln-EDTA series can be seen in the sums of ΔH_r , ΔS_r and ΔG_r data for Ln-EDTA formation and those for solution of the isomorphous Ln(III) ethylsulphate nonahydrate $[\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}]$. The importance of such combined data was discussed by Kawabe (2013b) for Ln-DTPA formation. The

combined reaction is as follows:



where n denotes the number of water molecules in the first-coordination sphere of Ln-EDTA. Because $\text{Ln}^{3+}_{(aq)}$ is eliminated in the combined reaction (1), the respective sums of ΔH_r , ΔS_r and ΔG_r are not affected by the hydration change of $\text{Ln}^{3+}_{(aq)}$ series at all. On the other hand, the Ln-EDTA formation is usually written in the form,



where the numbers of water molecules in the first coordination sphere of Ln^{3+} are not written explicitly. If such water molecules of Ln-EDTA like (1) are written, we have

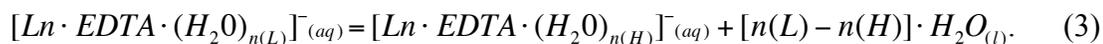


Even in (2'), the water molecules in the first coordination sphere of $\text{Ln}^{3+}_{(aq)}$ or $\text{EDTA}^{4-}_{(aq)}$ are not written explicitly, so that $n\text{H}_2\text{O}_{(l)}$ is nominally placed in the left-hand side of (2'). This is a matter of convention, and both (2) and (2') are acceptable equations in which explicit and implicit expressions for the water molecules in the inner sphere of Ln(III) species are adopted, respectively. In fact, the ΔH_r , ΔS_r and ΔG_r data for (2) listed in Table 1 involve the effects due to the hydration changes of both series of Ln-EDTA and light $\text{Ln}^{3+}_{(aq)}$, but those for (1) involve the effect only due to the hydration changes in Ln-EDTA series alone, because $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ are isomorphous in the entire Ln series (Kawabe, 1999a).

Figure 2 shows the series variations of thermodynamic data for the combined reactions of (1). The series change of ΔG_r may be given approximately by two linear

variations intersecting approximately at Eu. The series changes of ΔH_r and ΔS_r show similar step-like changes, the centers of which are also approximately at Eu. The plots of Fig. 2 strongly suggest that the hydration states of Ln-EDTA complex series are different between the light Ln (Ln=La to Nd) and heavy Ln (Ln=Dy to Lu), and that the intermediate members (Ln=Sm to Tb) are the mixtures of two distinguishable species of respective light and heavy Ln-EDTA series. Auxiliary solid lines of Fig. 2 are drawn in order to illustrate this situation with neglecting slightly curved features of the series variations. The plots of Fig. 2 are mostly compatible with the previous discussion by Geier and Karren (1971) and Ots (1973a, b).

The hydration change of the light Ln-EDTA series species relative to the heavy Ln-EDTA one is written by the reaction,



Hereafter we will write ΔG_r , ΔH_r , and ΔS_r for the reactions of (3) as $\Delta\Delta G_r$, $\Delta\Delta H_r$, and $\Delta\Delta S_r$, because they are given by the difference in ΔG_r , ΔH_r , and ΔS_r for the reaction (1) between the light Ln-EDTA and heavy Ln-EDTA series. Graphically they are given as the differences between respective pairs of linear curves for the light and heavy series in Fig. 2. The values of $\Delta\Delta S_r$ and $\Delta\Delta H_r$ at Eu are estimated to be roughly 70 J/mol/K and 20 kJ/mol, respectively. The $\Delta\Delta H_r$, and $\Delta\Delta S_r$ values from Fig. 2 may be important when we consider $\Delta n = n(L) - n(H)$, as will be discussed in the next subsection.

The thermodynamic data for Ln-EDTA formation with and without the corrections for the hydration changes of light $Ln^{3+}(aq)$ relative to heavy $Ln^{3+}(aq)$ of octahydrates (Kawabe, 1999a) are plotted in Fig. 3. The open circles are experimental data for light

Ln series without such corrections, and the filled circles are the corrected ones. Because the experimental data for the heavy Ln series (Ln=Tb to Lu) are unaffected by such corrections (Kawabe, 1999a), the open and filled circles in the range are the same in the plots of Fig. 3. Hence the data points of filled circles are for the reaction in the entire Ln series that

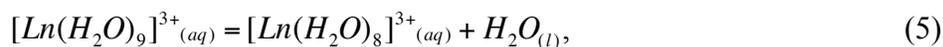


where $Ln^{3+}_{(octa, aq)}$ denotes octahydrate $Ln^{3+}_{(aq)}$. $Ln^{3+}_{(octa, aq)}$ is a real species in heavy Ln from Tb to Lu, but it is one component of $Ln^{3+}_{(aq)}$ as a mixture of nonahydrate and octahydrate of Ln^{3+} in light Ln from La to Gd (Kawabe, 1999a). The series variations of the data for (4) shown by filled circles are analogous to those of Fig. 2 for the reactions of (1). The values of $\Delta\Delta G_r$, $\Delta\Delta H_r$, and $\Delta\Delta S_r$ for the hydration reactions of (3) graphically estimated in Fig. 2 are also found in Fig.3, because the reactions of (3) are given by the differences between the reactions of (4) for heavy and light Ln series.

In Fig. 3, the corrections for the hydration change of light $Ln^{3+}_{(aq)}$ make the apparent break of ΔG_r and steps of ΔH_r and ΔS_r greater when compared with the uncorrected data. In particular, the experimental ΔG_r data indicate a more monotonous series change than the corrected ΔG_r data (Fig. 3). The hydration change of Ln-EDTA complex series is somewhat analogous to the hydration change of $Ln^{3+}_{(aq)}$ series (Kawabe, 1999a), and the overall effects of hydration changes in the two series on ΔG_r for Ln-EDTA complex formation are cancelled partly in light Ln.

3) Water molecules in the first-coordination spheres of two Ln-EDTA series

In the previous studies, for example, Geier and Karlen (1971) who accepted that $\text{Ln}^{3+}(\text{aq})$ are nonahydrates across the entire series, concluded that one water molecule is liberated in the reaction (3) with $\Delta n = n(\text{L}) - n(\text{H}) = 1$, but the different opinion claiming that four or three waters are liberated has been reported (Rizkalla and Choppin, 1991). Using $\Delta\Delta G_r$, $\Delta\Delta H_r$, and $\Delta\Delta S_r$ for the hydration reactions of (3) given in the plots of Figs. 2 and 3, we may discuss about $\Delta n = n(\text{L}) - n(\text{H})$. The hydration change effect in $\text{Ln}^{3+}(\text{aq})$ series is eliminated in Fig. 2, or it is separated from the series change of Ln-EDTA complexes in Fig. 3. The step-like changes of ΔS_r and ΔH_r are corresponding only to the hydration change between the two series of Ln-EDTA. In the plots of Figs. 2 and 3, the $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for the hydration reaction of (3) at Eu are approximately 70 J/mol/K and 20 kJ/mol, respectively. According to Kawabe (1999a) and Kawabe et al. (2006a,b), for the hydration change reaction of $\text{Ln}^{3+}(\text{aq})$ series that



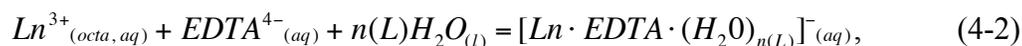
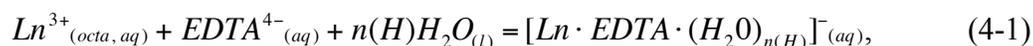
the values of $\Delta\Delta S_r$ and $\Delta\Delta H_r$ for (5) with $\text{Ln} = \text{Eu}$ are 33 J/mol/K and 10 kJ/mol, respectively. Miyakawa et al. (1988) reported similar values of $\Delta\Delta S_r = 34$ J/mol/K and $\Delta\Delta H_r = 15$ kJ/mol for (5) for $\text{Ln} = \text{Ce}$. The $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for Ln-EDTA are almost twice of those of $\text{Ln}^{3+}(\text{aq})$ series. If $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for (5) are accepted as meaningful reference values to infer the number of liberated water molecules in (3), it could be favored that $\Delta n = n(\text{L}) - n(\text{H}) = 2$ for (3) for the Eu member. More detailed discussion about this point will be given in **5**) and **6**) by referring to our thermodynamic model and the reported structural studies of crystalline hydrate salts of Ln-EDTA complexes, together with the results of luminescence kinetics and the lanthanide-induced

¹⁷O NMR shifts of Ln-EDTA cited above.

4) Thermodynamics of series changes of ΔG_r , ΔH_r , and ΔS_r for Ln-EDTA formation

The plots of Figs. 2 and 3 can illustrate the nature of hydration changes of Ln-EDTA across the series. However, the changes of ΔH_r and ΔS_r data for La, Ce, Pr, and Nd in Figs. 2 and 3 appear to show curvatures obviously. In Fig. 2, the linear variations of ΔH_r for middle Ln intersects that for heavy Ln at between Gd and Tb, but such linear trends of ΔS_r intersect at between Tb and Dy. The crossover positions are not the same between ΔH_r and ΔS_r . Similar discrepancies can also be found in Fig. 3. This must be inevitable as long as we are assuming linear variations with neglecting curved features of the series changes. In fact, there is no theoretical basis compelling us the linear variation trends in the plots of Figs. 2 and 3. Geier and Karlen (1971) plotted each thermodynamic quantity against the reciprocal of ionic radius of Ln^{3+} and discussed the series change properties, but this must be a conventional choice without the theoretical basis.

In order to overcome the semi-quantitative discussion as above or in the previous studies, we will consider the hydration change reactions of (3) for Ln-EDTA series with a more rigid thermodynamic treatment. The difference of the reactions of (4) with respect to two Ln-EDTA series,



gives the reaction (3) as noted above. Therefore, $\Delta\Delta G_r^0$ for (3), which is given by the

difference in the standard chemical potentials for the relevant species alone, can be expressed in terms of activities for the two Ln-EDTA species and water,

$$\Delta\Delta G_r^0 = -RT \ln \left[\frac{a(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})}) \cdot (a_w)^{n(\text{L})-n(\text{H})}}{a(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})} \right]. \quad (6)$$

When we assume that the activity coefficients for the two Ln-EDTA species are approximately the same, and that water activity (a_w) is approximately unity, eq. (6) can be expressed only by the ratio of molal concentrations of the two Ln-EDTA species:

$$\Delta\Delta G_r^0 \approx -RT \ln \left[\frac{m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})})}{m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})} \right] = RT \ln \left[\frac{m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})}{m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})})} \right]. \quad (7)$$

Hence the following three cases at T=298.15 K corresponding to the different ratios of molal concentrations in (7) are important:

- (i) $m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})/m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})}) > 99$: $\Delta\Delta G_r^0 > +11.4(\text{kJ/mol})$,
- (ii) $m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})/m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})}) = 1$: $\Delta\Delta G_r^0 = 0(\text{kJ/mol})$,
- (iii) $m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{L})})/m(\text{LnEDTA}(\text{H}_2\text{O})_{n(\text{H})}) < (1/99)$: $\Delta\Delta G_r^0 < -11.4(\text{kJ/mol})$.

When either $\Delta\Delta G_r^0 > +11.4(\text{kJ/mol})$ or $\Delta\Delta G_r^0 < -11.4(\text{kJ/mol})$, actually there exists only one Ln-EDTA species. But, when $-11.4(\text{kJ/mol}) \leq \Delta\Delta G_r^0 \leq +11.4(\text{kJ/mol})$, the two distinguishable Ln-EDTA species coexist in solution. The cases (i) is applicable to Ln-EDTA with Ln=La to Nd, and the case (iii) is to Ln-EDTA with Ln=Dy to Lu. The condition that $-11.4(\text{kJ/mol}) \leq \Delta\Delta G_r^0 \leq +11.4(\text{kJ/mol})$ is for Ln-EDTA with Ln=Sm to Tb, and the case (ii) is a special condition that two distinguishable Ln-EDTA species coexist with the same concentration. This special condition is approximately realizing at Eu-EDTA, and corresponding to the splitting of the (${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$) absorption spectra of

Eu-EDTA (Geier and Jørgensen, 1971). The series changes of ΔG_r in the plots of Figs. 2 and 3 are also illustrating this situation.

In order to discuss experimental data of ΔG_r , ΔH_r , and ΔS_r for middle Ln-EDTA complex formation, we have to describe the thermodynamic properties of a mixture of two distinguishable Ln-EDTA species. The chemical potentials for the two dissolved species are written as usual, respectively:

$$\bar{\mu}_{(L)} = \bar{\mu}_{(L)}^* + RT \ln a_{(L)} = \bar{\mu}_{(L)}^* + RT \ln[\gamma_{(L)} \cdot m_{(L)}], \quad (8-1)$$

$$\bar{\mu}_{(H)} = \bar{\mu}_{(H)}^* + RT \ln a_{(H)} = \bar{\mu}_{(H)}^* + RT \ln[\gamma_{(H)} \cdot m_{(H)}], \quad (8-2)$$

where the asterisk stands for the standard chemical potential at the condition that $m \rightarrow 1$ (mol/kg) in the infinite dilution at 298.15 K and 1 atm. The subscripts of L and H denote the light Ln-EDTA and heavy Ln-EDTA species, respectively. When the total molal concentrations of LnEDTA in solution is $m_{(total)}$, this is the sum of molal concentrations of the two distinguishable species of $m_{(L)}$ and $m_{(H)}$. The molal fractions of the two species are written in the following way:

$$x_{(L)} \equiv m_{(L)} / m_{(total)} \quad \text{and} \quad x_{(H)} \equiv m_{(H)} / m_{(total)}. \quad (9)$$

Then, eq. (7) is rewritten by using (8-1), (8-2), and (9),

$$\Delta \Delta G_r^0 \approx \bar{\mu}_{(H)}^* - \bar{\mu}_{(L)}^* + [n(L) - n(H)] \cdot \bar{\mu}_{(H_2O,l)}^0 \approx RT \ln \left[\frac{x_{(L)}}{x_{(H)}} \right] = RT \ln \left[\frac{1 - x_{(H)}}{x_{(H)}} \right], \quad (10)$$

where $\bar{\mu}_{(H_2O,l)}^0$ denotes the standard chemical potential for pure water. The experimental data are for Ln-EDTA with $m_{(total)}$ (mol/kg), but actually the solution is a mixture of two Ln-EDTA species for middle Ln. Hence, it follows that

$$\bar{\mu}_{(real\ sol)} = x_{(L)} \cdot \bar{\mu}_{(L)} + x_{(H)} \cdot \bar{\mu}_{(H)} = x_{(L)} \cdot \bar{\mu}_{(L)}^* + x_{(H)} \cdot \bar{\mu}_{(H)}^* + \Delta G_{mixing}, \quad (11)$$

where the last term of ΔG_{mixing} is the collection of concentration-dependent terms in (8-1) and (8-2) with the condition of $m_{(total)}(mol/kg)$,

$$\Delta G_{mixing} \approx [1 - x_{(H)}] \cdot RT \ln[1 - x_{(H)}] + x_{(H)} \cdot RT \ln x_{(H)}. \quad (12)$$

The enthalpy data for real Ln-EDTA solutions with $m_{(total)}(mol/kg)$ are given by using the partial molar enthalpies ($\bar{h}_{(L)}^*$ and $\bar{h}_{(H)}^*$) for the two Ln-EDTA species at the standard states with assuming ideal mixing,

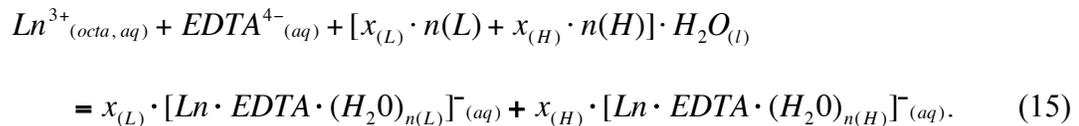
$$\bar{h}_{(real\ sol)} = x_{(L)} \cdot \bar{h}_{(L)}^* + x_{(H)} \cdot \bar{h}_{(H)}^* = [1 - x_{(H)}] \cdot \bar{h}_{(L)}^* + x_{(H)} \cdot \bar{h}_{(H)}^* , \quad (13)$$

The entropy data for real Ln-EDTA solutions with $m_{(total)}(mol/kg)$ are written by using (11), (12), and (13):

$$\begin{aligned} \bar{s}_{(real\ sol)} &= [\bar{h}_{(real\ sol)} - \bar{\mu}_{(real\ sol)}] / T \\ &= x_{(L)} \cdot [\bar{h}_{(L)}^* - \bar{\mu}_{(L)}^*] / T + x_{(H)} \cdot [\bar{h}_{(H)}^* - \bar{\mu}_{(H)}^*] / T - \Delta G_{(mixing)} / T \\ &= x_{(L)} \cdot \bar{s}_{(L)}^* + x_{(H)} \cdot \bar{s}_{(H)}^* - \Delta G_{(mixing)} / T, \end{aligned} \quad (14)$$

where $\bar{s}_{(L)}^*$ and $\bar{s}_{(H)}^*$ are the partial molar entropies for the two Ln-EDTA species at the standard states, and the ideal mixing is assumed. The expressions from (10) to (14) are the base of our thermodynamic model.

The reaction (4) is to be written as the linear combination of $x_{(L)}$ · (4-1) and $x_{(H)}$ · (4-2), because Ln-EDTA is a mixture:



The thermodynamic quantities for the reactions of (4) were written as $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ in Fig. 3. They can also be expressed in terms of (10)-(14) in

the following ways:

$$\begin{aligned} \Delta G_r(hyc) = & x_{(L)}\{\bar{\mu}_{(L)}^* - n(L) \cdot \bar{\mu}_{(H_2O)}^0\} + x_{(H)} \cdot \{\bar{\mu}_{(H)}^* - n(H) \cdot \bar{\mu}_{(H_2O)}^0\} + \Delta G_{mixing} \\ & - \bar{\mu}^*(Ln^{3+}, octa aq) - \bar{\mu}^*(EDTA^{4-}, aq), \end{aligned} \quad (16-1)$$

$$\begin{aligned} \Delta H_r(hyc) = & x_{(L)}\{\bar{h}_{(L)}^* - n(L) \cdot \bar{h}_{(H_2O)}^0\} + x_{(H)} \cdot \{\bar{h}_{(H)}^* - n(H) \cdot \bar{h}_{(H_2O)}^0\} \\ & - \bar{h}^*(Ln^{3+}, octa aq) - \bar{h}^*(EDTA^{4-}, aq), \end{aligned} \quad (16-2)$$

$$\begin{aligned} \Delta S_r(hyc) = & x_{(L)}\{\bar{s}_{(L)}^* - n(L) \cdot \bar{s}_{(H_2O)}^0\} + x_{(H)} \cdot \{\bar{s}_{(H)}^* - n(H) \cdot \bar{s}_{(H_2O)}^0\} - \Delta G_{mixing} / T \\ & - \bar{s}^*(Ln^{3+}, octa aq) - \bar{s}^*(EDTA^{4-}, aq), \end{aligned} \quad (16-3)$$

Note that (16-1), (16-2), and (16-3) are valid even for the case of $\Delta \Delta G_r^0 > +11.4(kJ/mol)$. Putting $x_{(L)} \approx 1$ and $x_{(H)} \approx 0$ into them, we have the

following results:

$$\Delta G_r(hyc) = \bar{\mu}_{(L)}^* - n(L) \cdot \bar{\mu}_{(H_2O)}^0 - \bar{\mu}^*(Ln^{3+}, octa aq) - \bar{\mu}^*(EDTA^{4-}, aq), \quad (17-1)$$

$$\Delta H_r(hyc) = \bar{h}_{(L)}^* - n(L) \cdot \bar{h}_{(H_2O)}^0 - \bar{h}^*(Ln^{3+}, octa aq) - \bar{h}^*(EDTA^{4-}, aq), \quad (17-2)$$

$$\Delta S_r(hyc) = \bar{s}_{(L)}^* - n(L) \cdot \bar{s}_{(H_2O)}^0 - \bar{s}^*(Ln^{3+}, octa aq) - \bar{s}^*(EDTA^{4-}, aq), \quad (17-3)$$

where all the partial molar quantities for the heavy Ln-EDTA species are absent. The three expressions can also be written directly from the reaction (4-1). Likewise, for Ln-EDTA with Ln=Ho to Lu and $\Delta \Delta G_r^0 < -11.4(kJ/mol)$, the condition that $x_{(L)} \approx 0$ and $x_{(H)} \approx 1$ for (16-1), (16-2), and (16-3) give the following equations,

$$\Delta G_r(hyc) = \bar{\mu}_{(H)}^* - n(H) \cdot \bar{\mu}_{(H_2O)}^0 - \bar{\mu}^*(Ln^{3+}, octa aq) - \bar{\mu}^*(EDTA^{4-}, aq), \quad (18-1)$$

$$\Delta H_r(hyc) = \bar{h}_{(H)}^* - n(H) \cdot \bar{h}_{(H_2O)}^0 - \bar{h}^*(Ln^{3+}, octa aq) - \bar{h}^*(EDTA^{4-}, aq), \quad (18-2)$$

$$\Delta S_r(hyc) = \bar{s}_{(H)}^* - n(H) \cdot \bar{s}_{(H_2O)}^0 - \bar{s}^*(Ln^{3+}, octa aq) - \bar{s}^*(EDTA^{4-}, aq), \quad (18-3)$$

Since the partial molar quantities for H₂O(l) and EDTA⁴⁻(aq) are constant across the Ln

series, the series changes of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ in Fig. 3 are given by those of partial molar quantities for the two Ln-EDTA species and for $\text{Ln}^{3+}(\text{octa}, \text{aq})$, and $x_{(L)} (= 1 - x_{(H)})$ and $x_{(H)}$. The values of $x_{(L)} (= 1 - x_{(H)})$ and $x_{(H)}$ can be obtained by solving (10) by using a graphically estimated value of $\Delta\Delta G_r^0$.

$\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for light Ln-EDTA given by (17-1), (17-2), and (17-3) or those for heavy Ln-EDTA given by (18-1), (18-2), and (18-3) can be written as $\Delta G_r^0(hyc)$, $\Delta H_r^0(hyc)$, and $\Delta S_r^0(hyc)$, because they involve only the partial molar quantities at the standard states. But this is not allowed in $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for middle Ln-EDTA given by (16-1), (16-2), and (16-3), because they involve the terms related to $x_{(L)} (= 1 - x_{(H)})$ and $x_{(H)}$. Hence we will use $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ without the superscript "0" for all Ln-EDTA in this context hereafter. However, we will use the superscript "0" in $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ for the hydration reaction (3) given by the differences of [(18-1)-(17-1)], [(18-2)-(17-2)], and [(18-3)-(17-3)], respectively. In the preceding subsections, we wrote that $\Delta\Delta G_r$, $\Delta\Delta H_r$, and $\Delta\Delta S_r$ for the hydration reactions (3) are graphically estimated in Fig. 2 and Fig.3. But, in the correct expressions hereafter, $\Delta\Delta G_r$, $\Delta\Delta H_r$, and $\Delta\Delta S_r$ are to be replaced by $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$.

Notice that $\Delta G_r(hyc)$ of (16-1) and $\Delta S_r(hyc)$ of (16-3) involve ΔG_{mixing} and $-\Delta G_{mixing}/T$, respectively. The thermodynamic data for a mixed solution of Ln-EDTA with $m_{(total)}$ (mol/kg) involve the terms relating to ΔS_{mixing} in $\Delta G_r(hyc)$ and $\Delta S_r(hyc)$: $\Delta G_{mixing} = -T\Delta S_{mixing}$ and $\Delta S_{mixing} = -\Delta G_{mixing}/T$, respectively. The case (ii)

that $m(\text{LnEDTA}(\text{H}_2\text{O})_{n(L)})/m(\text{LnEDTA}(\text{H}_2\text{O})_{n(H)}) = 1$, namely, $x_{(L)} = x_{(H)} = 1/2$ and $\Delta\Delta G_r^0 = 0$, can illustrate the importance of $\Delta S_{\text{mixing}} = -\Delta G_{\text{mixing}}/T = R\ln 2$, which is the maximum mixing entropy in the binary ideal mixture.

In this way, the equations of (16-1), (16-2), and (16-3) are the thermodynamic expressions for the series variations of $\Delta G_r(\text{hyc})$, $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ as shown in Fig. 3. All the terms in (16-1), (16-2), and (16-3) are given by (17-1) and (17-2) for light Ln-EDTA series and by (18-1) and (18-2) for heavy Ln-EDTA series, and (8) as to $\Delta\Delta G_r^0$ given as [(18-1)-(17-1)].

5) Calculations of ΔG_r , ΔH_r , and ΔS_r for middle Ln-EDTA complex formations

The $\Delta G_r(\text{hyc})$, $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ values have been calculated for middle Ln(III)-EDTA complexes (Fig. 4). The $\Delta G_r(\text{hyc})$ values for the two species series of middle Ln-EDTA complexes (open circles) have been estimated by extending the experimental data (filled circles) according to (17-1) and (18-1). There are two important constraints in estimating the data points of open circles: (a) the two series changes of $\Delta G_r(\text{hyc})$ intersect approximately at Eu, namely, $\Delta\Delta G_r^0 \approx 0$ at Eu, and (b) the series change of experimental data (filled circles) suggest that $\Delta\Delta G_r^0 = +11.4$ (kJ/mol) at around Nd, and $\Delta\Delta G_r^0 = -11.4$ (kJ/mol) at around Dy as shown by the two arrows in Fig. 4. Each pair of open and filled circles for $\Delta G_r(\text{hyc})$ in Fig. 4 gives the estimate of $\Delta\Delta G_r^0$, and then $x_{(L)} (= 1 - x_{(H)})$ and $x_{(H)}$ can be known by solving (10) with the $\Delta\Delta G_r^0$ value. The data points of crosses for $\Delta G_r(\text{hyc})$ in Fig. 4 have been calculated for the middle Ln series by using (16-1). The values of $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ in middle

Ln series have also been calculated in analogous ways to $\Delta G_r(hyc)$ according to (16-2) and (16-3).

Calculations on a trial and error basis were repeated until the results shown in Fig. 4 were obtained. The individual values are listed in Part A of Table 3. The standard deviations of calculated values of $\Delta G_r(hyc)$ and $\Delta H_r(hyc)$ from the experimental ones for Sm, Eu, Gd, and Tb are approximately 0.2 kJ/mol and 0.4 kJ/mol, respectively. The calculated values (crosses) of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ are in good agreements with experimental data (filled circles) in Fig. 4. Note that such good agreements could not be obtained if small curvatures of the series changes seen in Figs. 2 and 3 were ignored. A fairly large tetrad effect with convexity is partly visible in the $\Delta H_r(hyc)$ data for the light Ln-EDTA series, whereas a small concave tetrad effect may possibly be present in those for the heavy Ln-EDTA series.

The results of Fig. 4 are based on the experimental ΔH_r data by Mackey et al. (1962) and those ΔG_r data accepted by Kawabe (2013a). The $\Delta\Delta S_r^0$ and $\Delta\Delta H_r^0$ values at Eu in Fig. 4 are +66 (J/mol/K) and +20 (kJ/mol), respectively. They are approximately the same as those estimated graphically in Figs. 2 and 3 assuming linear trends. On the other hand, Geier et al. (1969) measured the (${}^7F_0 \rightarrow {}^5L_6$) absorption band with two peaks at 395 and 394 nm of Eu^{3+} of Eu(III)-EDTA solution from 2 to 81°C, and they evaluated the $\Delta\Delta S_r^0$ and $\Delta\Delta H_r^0$ values for the reaction (3) with Ln=Eu: $\Delta\Delta S_r^0 = +(59 \pm 13)$ (J/mol/K) and $\Delta\Delta H_r^0 = +(18 \pm 4)$ (kJ/mol). Similarly, Graeppi et al. (1995) analyzed the splitting of (${}^7F_0 \rightarrow {}^5D_0$) absorption band of Eu^{3+} of Eu(III)-EDTA solution at 580 nm, and they reported that $\Delta\Delta S_r^0 = +(54.9 \pm 1.6)$ (J/mol/K) and $\Delta\Delta H_r^0 = +(17.7 \pm 0.5)$ (kJ/mol). The

spectroscopic results are comparable with our estimates of the thermodynamic parameters for the hydration change reaction (3) with Ln= Eu.

Graeppi et al. (1995) also determined the volume change of $\Delta\Delta V_r^0 = +(13.2\pm 0.2)$ (cm^3/mol) for the reaction (3) at Ln=Eu from the ratio of two splitting peaks at 580 nm as a function of pressure (0.1 ~ 200 MPa). They argued that the volume change is reasonable as the loss of one inner-sphere water molecule, and compared it with another experimental example of volume change of +10.9 (cm^3/mol) for $[\text{Ce}(\text{H}_2\text{O})_9]^{3+}_{(aq)} = [\text{Ce}(\text{H}_2\text{O})_8]^{3+}_{(aq)} + \text{H}_2\text{O}_{(l)}$ (Laurenzy and Merbach, 1988), which was also derived from the pressure change of the absorption spectra for aqueous $\text{Ce}(\text{ClO}_4)_3$ solution at 295 nm. Graeppi et al. (1995) also referred to the calculated difference in partial molar volume of +12.6 (cm^3/mol) between the 9- and 8-coordination $\text{Eu}^{3+}_{(aq)}$ based on a semi-empirical formula by Swaddle (1983). Thus the volume change of $+(13.2\pm 0.2)$ (cm^3/mol) by Graeppi et al. (1995) may suggest that $\Delta n = n(L) - n(H) = 1$ for Eu-EDTA solution.

The numbers of water molecules in the inner coordination spheres of middle Ln-EDTA can be calculated as $n = x_{(L)} \cdot n(L) + x_{(H)} \cdot n(H)$ in our thermodynamic model. The numbers of water molecules in the inner hydration spheres of middle Ln-EDTA have been calculated as $n = x_{(L)} \cdot n(L) + x_{(H)} \cdot n(H)$ by assuming the values of n(L) and n(H) for the three cases:

- (a) n(L)=4, n(H)=2: n(Sm-EDTA)=3.6, n(Eu-EDTA)=3.0, n(Tb-EDTA)=2.2
- (b) n(L)=3, n(H)=2: n(Sm-EDTA)=2.8, n(Eu-EDTA)=2.5, n(Tb-EDTA)=2.1 (19)
- (c) n(L)=3, n(H)=1: n(Sm-EDTA)=2.6, n(Eu-EDTA)=2.0, n(Tb-EDTA)=1.2

n(Dy-EDTA) is always equal to the assumed values of n(H). Our values of

$n = x_{(L)} \cdot n(L) + x_{(H)} \cdot n(H)$ correspond to the experimental values of water molecules (q_w) in the inner hydration spheres of middle Ln-EDTA by the luminescence decay constants studies. The case (b) with $n(L)=3$ and $n(H)=2$ gives better agreements with the estimates for Eu-EDTA and Tb-EDTA by the luminescence decay constants than the other cases of (a) and (c): We have summarized the results by five different research groups that $q_w(\text{mean})=2.6$ for Eu-EDTA as above. Although $q_w(\text{Tb-EDTA}) = 2.6 \pm 0.5$ (Rizkalla and Choppin, 1991; Braittain et al., 1992); 2.4 ± 0.3 (Kimura and Kato, 1998); 2.9 ± 0.3 (Beeby et al., 1999) have been reported, the majority of luminescence decay constant measurements strongly indicates that $2 < n(\text{Tb-EDTA}) < 3$, therefore we conclude that the case (b) of $n(L)=3$, $n(H)=2$, and $\Delta n=1$ is the most acceptable as the hydration change reaction (3). The case (b) is also compatible with the conclusion by Caravan et al. (1997) from the lanthanide-induced ^{17}O shifts of D_2O for aqueous Ln-EDTA complexes that the light Ln-EDTA series (Ln=Pr, Nd, and Eu) has $q_w=2.5$ and heavy Ln-EDTA series (Ln=Tb~Yb) does $q_w=2.0$.

Thus, the hydration numbers of middle Ln-EDTA, $n = x_{(L)} \cdot n(L) + x_{(H)} \cdot n(H)$, in our thermodynamic model with $n(L)=3$ and $n(H)=2$, are comparable with the estimates by their luminescence kinetics and the lanthanide-induced ^{17}O shifts of D_2O . The experimental result of $\Delta\Delta V_r^0 = +(13.2 \pm 0.2)$ (cm^3/mol) for the reaction (3) with Ln=Eu (Graeppi et al., 1995) is in favor of $\Delta n = n(L) - n(H) = 1$.

We have pointed out in **3**) that $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for the hydration change reaction (3) for Ln-EDTA are almost twice of those of hydration change reaction (5) for light $\text{Ln}^{3+}(\text{aq})$ series, and raised a question whether or not such $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for (3)

of Ln-EDTA suggest that $\Delta n = n(L) - n(H) = 2$ in (3). The answer is now clearly given: We conclude that $\Delta n = n(L) - n(H) = 1$ in (3), so that the $\Delta\Delta S_r$ and $\Delta\Delta H_r$ values for the hydration change reaction (5) for light $\text{Ln}^{3+}(\text{aq})$ series should not be understood as reference values in order to infer the number of liberated water molecules like (3).

The condition of $n(L)=3$, $n(H)=2$, and $\Delta n=1$ is eventually the same as the assumption for Eu-EDTA made by Graeppi et al. (1995) from an analogy of the series change of water molecules in crystalline hydrate of Ln-EDTA complexes. We will inspect the hydration states of Ln^{3+} in crystalline hydrate salts of Ln-EDTA complexes in the next.

6) Hydrated Ln(III) in Ln-EDTA complexes: crystalline hydrate salts vs. solution

The coordination states of Ln^{3+} in crystalline hydrate salts of Ln-EDTA complexes are interesting to consider those in solution. Structural studies of the hydrate salts of $M[\text{Ln(III)} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_n] \cdot m\text{H}_2\text{O}$ with different monovalent cations ($M=\text{H}$, Na, K, and Cs), have been reported by X-ray and neutron diffraction methods (Lind et al., 1965; Hoard et al., 1965; Nassimbeni et al., 1979; Templeton et al., 1982; Engel et al., 1985; Nakamura et al., 1995; Sakagami et al., 1999 and references therein). The coordination numbers (CN) of Ln^{3+} in crystalline hydrate salts are CN=10 of $[\text{LaEDTA}(\text{H}_2\text{O})_4]^-$ with $M=\text{H}$ (Lind et al., 1965), CN=9 of $[\text{LnEDTA}(\text{H}_2\text{O})_3]^-$ for $\text{Ln}=\text{La}$, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er with $M=\text{Na}$, K or Cs, CN=8 of $[\text{LnEDTA}(\text{H}_2\text{O})_2]^-$ for $\text{Ln}=\text{Dy}$, Ho, and Yb with $M=\text{Cs}$ or K. Sakagami et al. (1999) reported the interesting results that CN=9 is realized in the Na and K hydrate salts of Dy- and Ho-EDTA complexes, whereas CN=8 is observed in the Cs hydrate salts of Dy- and Ho-EDTA complexes.

Thus the number of water molecules in the inner coordination spheres of Ln^{3+} in $M[\text{LnEDTA}(\text{H}_2\text{O})_n] \cdot m\text{H}_2\text{O}$ depends on the monovalent cation of M^+ as well as Ln^{3+} . Therefore, the hydration change behavior across crystalline hydrate salt series may not be so analogous to that in aqueous Ln(III)EDTA series. Our estimate of $n(\text{H})=2$ with $\text{CN}=8$ for the aqueous heavy Ln-EDTA series is similar to $\text{CN}=8$ in the hydrate salts of $[\text{LnEDTA}(\text{H}_2\text{O})_2]^-$ with heavy Ln of Dy, Ho, and Yb, and $n(\text{L})=3$ with $\text{CN}=9$ for LnEDTA in solution is comparable with the majority of hydrate salts of $[\text{LnEDTA}(\text{H}_2\text{O})_3]^-$ for light and middle Ln . This situation suggests some systematic difference in the structural behavior of Ln(III)-EDTA complex between aqueous solution and crystalline hydrate salts, although it is certain that three to two water molecules present in the first-coordination spheres of Ln^{3+} commonly stabilize the Ln-EDTA complexes in both solution and hydrate salts.

Durand et al. (2000) reported a molecular dynamics (MD) study of alkali-earth and lanthanide complexes with EDTA in aqueous solution, and suggested that there are three water molecules in inner coordination spheres of Ln-EDTA in solution for $\text{Ln}=\text{La}$ and Eu but two water molecules in the case of $\text{Ln}=\text{Lu}$. Although their suggestion is qualitative, hydration states of Ln(III)-EDTA in solution might be analogous to those observed in crystalline hydrate salts of Ln-EDTA . The coordination states of Ln(III) in $M[\text{Ln(III)} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_n] \cdot m\text{H}_2\text{O}$ and the MD calculation on the inner coordination sphere of Ln-EDTA in solution, may give support the condition of $n(\text{L})=3$ and $n(\text{H})=2$ with $\Delta n(\text{H}_2\text{O})=1$.

Accordingly, such a condition that $n(\text{L})=3$ and $n(\text{H})=2$ with $\Delta n(\text{H}_2\text{O})=1$ for the

hydration change of Ln(III) in Ln-EDTA solution, can be acceptable from 1) the hydration numbers by luminescence spectroscopy, 2) the pressure change of splitting peaks of (${}^7F_0 \rightarrow {}^5D_0$) absorption bands of Eu^{3+} of Eu(III)-EDTA solution, 3) the lanthanide-induced ${}^{17}\text{O}$ MNR shifts, 4) a molecular dynamics (MD) study, and 5) our thermodynamic model. Hence, we may rewrite the hydration change reaction (3) between $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_{n(L)}]_{(aq)}^-$ and $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_{n(H)}]_{(aq)}^-$ in the form with $n(L) = 3$, $n(H) = 2$ and $\Delta n(\text{H}_2\text{O}) = 1$,



This understanding will be kept in mind in the subsequent discussion as to the nephelauxetic effect relating to the change of coordination number of Ln^{3+} in Ln-EDTA species in solution.

7) Nephelauxetic effect relating to the change of coordination number of Ln^{3+}

Kawabe (2013a) confirmed the Gd-break with a small tetrad-like variation in the series change of $\log K(\text{Ln-EDTA})$, and he noted that the tetrad-like variation in the light Ln is less obvious than in the heavy Ln. He suggested that the effects due to the hydration changes of both light $\text{Ln}^{3+}(\text{aq})$ and middle Ln-EDTA series are cancelled partly in the light Ln series. The plots of $\Delta G_r(\text{hyc})$, $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ of Fig. 4, which are free from the hydration change of light $\text{Ln}^{3+}(\text{aq})$, illustrate that the observed Gd break in $\Delta G_r = -RT \ln K(\text{Ln-EDTA})$ does represent the hydration change between $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_3]_{(aq)}^-$ and $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]_{(aq)}^-$ in the middle of Ln series. This can also explain the reason why $\log K(\text{Ln-EDTA})$ data exhibit such an asymmetrical

tetrad effect across the entire Ln. The plots of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ in Fig. 4 for Ln= Dy~Lu are for the reactions of (4-1) with n(H)=2:



Those plots for Ln=La~Sm are for the reactions of (4-2) with n(L)= 3:



There is an important difference between (20-1) and (20-2) in that the coordination number (CN) of Ln^{3+} is unchanged in (20-1) whereas it does change in (20-2) from CN=8 to CN=9. The increase of CN makes the average distance between Ln^{3+} and ligands greater, and may reduce the covalency of bonding between Ln(III) and ligands. The unchanged CN in (20-1) and the increase of CN in (20-2), may account for the asymmetrical tetrad effect in $\log K(Ln-EDTA)$ across the entire Ln series (Kawabe, 2013a).

The $\Delta H_r(hyc)$ values for the light Ln-EDTA series are for the reaction (20-2) in which the coordination number (CN) of Ln^{3+} increases from 8 to 9. Hence it is expected that the light Ln-EDTA series have larger Racah parameters than $Ln^{3+}_{(octa, aq)}$, and the $\Delta H_r(hyc)$ values may show a convex tetrad effect according to the nephelauxetic effect relating to the CN change of Ln^{3+} (Reisfeld and Jørgensen, 1977; Jørgensen, 1979; Kawabe et al., 2006b). This seems consistent with the convex curvature of $\Delta H_r(hyc)$ in the part of La, Ce, Pr, and Nd and a small depression at Gd in Fig. 4. On the other hand, CN of Ln^{3+} is unchanged in the reaction (20-1) for the formation of heavy Ln-EDTA series, and then the Racah parameters of the heavy Ln-EDTA series may be comparable with those of $Ln^{3+}_{(octa, aq)}$. A smooth variation with or without a minor tetrad effect is

expected in the $\Delta H_r(\text{hyc})$ data for the heavy Ln-EDTA series. This seems to be compatible with the plots of Fig. 4.

The thermodynamic data for the hydration change reaction of Ln-EDTA species given by the reaction (3) or (3') are also important in view of the nephelauxetic effect due to the CN change of Ln^{3+} . The CN of Ln^{3+} decreases from 9 to 8 in the hydration change reaction (3'), because the CN of Ln^{3+} in the light and heavy Ln-EDTA series are 9 and 8, respectively. The smaller CN of Ln^{3+} means the smaller average Ln-ligand distance, and then the smaller Racah parameters (Reisfeld and Jørgensen, 1977; Jørgensen, 1979; Kawabe et al., 2006b), hence we expect a concave tetrad effect in the series variation of $\Delta\Delta H_r^0$ for the reaction (3) or (3'). The three sets of thermodynamic quantities for the reactions of (20-1), (20-2), and (3') are characterized by the CN changes of Ln^{3+} , (ΔCN) = 0, +1, and -1, respectively. Because (3') is given by (20-1) minus (20-2), the thermodynamic quantities for (3') are constrained by the differences between those for (20-1) and (20-2).

In Fig. 4, the La, Ce, and Pr data points of $\Delta G_r(\text{hyc})$, $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ for the reaction (20-1) of heavy Ln-EDTA complexes are not plotted. Similarly, the Ho, Er, Tm, and Lu points for (20-2) are not plotted. These data points cannot be estimated only by the thermodynamic equations mentioned above. Nevertheless, it is possible to estimate such data points by assuming the improved RSPET equation (Kawabe, 1992) as in the case of Ln-DTPA formation (Kawabe, 2013b). If the series changes of $\Delta G_r(\text{hyc})$, $\Delta H_r(\text{hyc})$, and $\Delta S_r(\text{hyc})$ for (20-2) given by (17-1), (17-2), and (17-3) and those for (20-1) given by (18-1), (18-2), and (18-3) are estimated in the full range of Ln series,

and then the series changes of $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ for (3') are also given eventually. The estimated series changes of thermodynamic quantities for (20-1), (20-2) and (3') may involve tetrad effect variations due to the nephelauxetic effects relating to the ΔCN values of 0, +1, and -1, respectively. The plots of Fig. 4 can be extended into the full range of the Ln series by using the RSPET equation in the next.

8) Least-squares regressions of thermodynamic data by RSPET equation

The data points of La, Ce, and Pr of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for the heavy Ln-EDTA series and those of Ho, Er, Tm, and Lu for light Ln-EDTA series can be estimated graphically from the plots of Fig. 4, and from the partly known series changes of $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ values for the reaction (3'). Their series changes are once known in the full range of Ln series by the graphical estimates, then they are regressed by the improved RSPET equation (Kawabe, 1992) by the method of least squares. The cycle of graphical extension of data points followed by their least-square fitting to the RSPET equation, was repeated until a satisfactory data set was obtained. As a matter of fact, the estimated values in Fig. 4 are a part of such values derived from this procedure using RSPET. The values of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for (20-1) and (20-2) in the full range of Ln series are listed in Part A of Table 2, are the thermodynamic quantities which are those for the reactions involving only single species of $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$ or $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)}$. Therefore, they agree with the experimental values written in *gothic* for light Ln (La~Nd) or heavy Ln (Dy~Lu). Comparison between the experimental and calculated ones in the middle Ln-EDTA is

made in Part A of Table 3. The coexistence of two distinct Ln-EDTA hydrates is treated by (16-1), (16-2), and (16-3). The results of Tables 2 and 3 are graphically shown in Fig. 5, together their regressions by the RSPET equation.

The calculations have been obtained using the experimental data of ΔH_r by Mackey et al. (1962) and ΔG_r by Kawabe (2013a) on the basis of eqs. (10), (16-1), (16-2), (16-3) and the others described above. The resultant values of $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ for (3') are given in Part B of Table 2, and their regressions by the RSPET equation are listed in Part B of Table 3. They are also plotted graphically in Fig. 6.

The improved RSPET equation (Kawabe, 1992) is given in the form,

$$\Delta Y(q) = [(a + bq) qZ^* + c] + (9/13)n(S)C_1Z^* + m(L)C_3Z^*, \quad (21)$$

where $\Delta Y(q)$ denotes $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, $\Delta S_r(hyc)$, $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, or $\Delta\Delta S_r^0$, and q stands for the number of 4f electrons in the electronic configuration $[\text{Xe}](4f)^q$ for Ln^{3+} . The effective nuclear charge ($Z^*=Z-S_f$) for 4f electrons of Ln^{3+} is given by $(q+25)$. The first term in (21) is for the smooth variation component of $\Delta Y(q)$. The second and third terms in (21) are for the octad and intrinsic tetrad effects, respectively. The overall tetrad effect of $\Delta Y(q)$ is given by the sum of the second and third terms. The constant coefficients of $n(S)$ and $m(L)$ are the theoretical ones associated with the energy contributions by Racah E^1 and E^3 parameters, in which S and L denote the total spin and orbital quantum numbers for the ground term (^{2S+1}L) of Ln^{3+} , respectively. The values of $n(S)$ and $m(L)$ are given in Kawabe (1992). The parameters of a , b , c , C_1 , and C_3 are the constant coefficients determined in the least-squares fitting of $\Delta Y(q)$.

Originally the improved RSPET equation was proposed for the ΔH_r data (Kawabe,

1992), but it has been found that this equation is applicable to the data of $\Delta G_r (= -2.303RT \log K)$ (Kawabe, 1999a, b, c; Ohta and Kawabe, 2000a, b and 2001; Kawabe and Masuda, 2001). Eventually the series change of entropy data can also be described by eq. (21), because of the linear relation that $\Delta S_r = (\Delta H_r - \Delta G_r)/T$. This has been confirmed by using the experimental data for solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ and $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ with $n=7$ and 6 (Kawabe, 1999a) and for Ln -DTPA complex formations (Kawabe, 2013b). The improved RSPET equation (21) means that the thermodynamic quantities are to be plotted against $q (=Z-57)$.

When the data of $\Delta H_r(\text{hyc})$ are input into $\Delta Y(q)$ of (21), the Racah E^1 and E^3 parameters of Ln -EDTA relative to octahydrate $\text{Ln}^{3+}(\text{aq})$ are given as

$$\Delta E^1 = C_1(q+25) \quad \text{and} \quad \Delta E^3 = C_3(q+25). \quad (22)$$

When the $\Delta \Delta H_r^0$ data for the reaction (3') are input, the Racah E^1 and E^3 parameters of $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]^- (\text{aq})$ relative to $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_3]^- (\text{aq})$ are obtained according to (22). However, when eq. (21) is applied to the data of $\Delta G_r(\text{hyc})$, $\Delta S_r(\text{hyc})$, $\Delta \Delta G_r^0$, or $\Delta \Delta S_r^0$, the resultant C_1 and C_3 cannot be interpreted like (22), but they are phenomenological parameters describing the octad and intrinsic tetrad effect variations, respectively.

Since eq. (21) can be written in such a way that

$$\Delta Y(q) = \Delta Y(\text{sm}) + \Delta Y(\text{tetrad}), \quad (23)$$

where $\Delta Y(\text{sm})$ and $\Delta Y(\text{tetrad})$ denote the smooth and tetrad effect variations given by $[(a+ bq)qZ^* + c]$ and $[(9/13)n(\text{S})C_1Z^* + m(\text{L})C_3Z^*]$, respectively. Because of the general relation that $\Delta G = \Delta H - T\Delta S$, the following thermodynamic relations with respect

to the smooth and tetrad effect components hold true as long as all the data sets of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, $\Delta S_r(hyc)$ are described by eq. (21):

$$\Delta G_r(sm) = \Delta H_r(sm) - T\Delta S_r(sm), \quad (24)$$

$$\Delta G_r(tetrad) = \Delta H_r(tetrad) - T\Delta S_r(tetrad). \quad (25)$$

Equation (25) is an important constraint as to the tetrad effect variations of the thermodynamic quantities of ΔG . They are expressed by means of C_1 or C_3 parameter values as discussed in Kawabe (2013b),

$$C_1(\Delta G_r) = C_1(\Delta H_r) - TC_1(\Delta S_r) \quad \text{and} \quad C_3(\Delta G_r) = C_3(\Delta H_r) - TC_3(\Delta S_r). \quad (26)$$

The C_1 or C_3 parameter values determined by using (21) are summarized in Table 4, in which it is shown that the relationships of (26) hold true.

The respective differences in $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ between (20-1) and (20-2) give $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ values for (3'), so that the C_1 and C_3 parameters for the series changes of $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ are also given by the differences in C_1 and C_3 parameters between the respective pairs of $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for the two isomorphous Ln-EDTA formation series. Table 4 shows that the C_1 and C_3 parameters calculated from those C_1 and C_3 values for $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ are in good agreement with those values determined directly in the least-squares fitting of $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ to (21). The improved RSPET equation can be successfully applied to $\Delta G_r(hyc)$, $\Delta H_r(hyc)$, and $\Delta S_r(hyc)$ for the complex formations of two Ln-EDTA series of (20-1) and (20-2), and to $\Delta\Delta G_r^0$, $\Delta\Delta H_r^0$, and $\Delta\Delta S_r^0$ for the hydration change reaction (3') as well.

9) Different Racah parameters between two Ln(III)-EDTA series

The experimental ΔH_r data by Mackey et al. (1962) combined with the recently compiled data of ΔG_r data by Kawabe (2013a) lead to the results shown in Figs. 4, 5 and 6. The faint concave tetrad effect in $\Delta H_r(\text{hyc})$ for the reaction (20-1) of the heavy Ln-EDTA series is contrasting to the large convex tetrad effect in $\Delta H_r(\text{hyc})$ for the reaction (20-2) of light Ln-EDTA series (Fig. 5). Also, the series change of $\Delta\Delta H_r^0$ for the reaction (3') obviously indicates a large concave tetrad effect (Fig. 6). The relative Racah (E^1 and E^3) parameter values for Nd^{3+} ($q=3$) in $\Delta H_r(\text{hyc})$ for the reactions of (20-1) and (20-2) and $\Delta\Delta H_r$ for the reaction (3'), have been calculated by using C_1 and C_3 parameter values listed in Tables 3 and 4 and eq. (22). The calculations are summarized in Table 6. With going from the $\Delta H_r(\text{hyc})$ data for (20-2) to those for (20-1), and then to the $\Delta\Delta H_r^0$ data for (3'), the $\Delta E^1(\text{Nd}^{3+})$ value decreases from $+39 \text{ cm}^{-1}$ ($\Delta\text{CN}=+1$), -19 cm^{-1} ($\Delta\text{CN}=0$), and then to -58 cm^{-1} ($\Delta\text{CN}=-1$). Similarly, the $\Delta E^3(\text{Nd}^{3+})$ value also decreases from $+8 \text{ cm}^{-1}$ ($\Delta\text{CN}=+1$), -4 cm^{-1} ($\Delta\text{CN}=0$), and then to -12 cm^{-1} ($\Delta\text{CN}=-1$). This must be the nephelauxetic effect correlating with the decrease of coordination number (CN) of Ln^{3+} , in which the average distance between Ln^{3+} and ligands decreases with the decreasing CN, and then the increased covalency of Ln^{3+} -ligand bonding makes the Racah parameters smaller (Reisfeld and Jørgensen, 1977; Tröster, 2003; Kawabe et al., 2006b).

In the case of $\Delta H_r(\text{hyc})$ data for (20-1) with $\Delta\text{CN}=0$, the respective negative $\Delta E^1(\text{Nd}^{3+})$ and $\Delta E^3(\text{Nd}^{3+})$ values of -19 cm^{-1} and -4 cm^{-1} mean that the average Ln^{3+} -ligand bonding in $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]_{(aq)}^-$ is slightly more covalent than that in $\text{Ln}^{3+}_{(\text{octa},aq)}$.

This may correspond to the slightly covalent anionic ligand of EDTA⁻⁴ relative to H₂O, not to the nephelauxetic effect relating to the CN change of Ln³⁺.

The ΔH_r data for Ln-EDTA formations by Mackey et al. (1962) are the thermochemical evidence for the significantly larger Racah (E^1 and E^3) parameters of the light Ln-EDTA series of $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)}$ relative to those in the heavy Ln-EDTA series of $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$. Note that this can be revealed only when the hydration changes of both series of light $Ln^{3+}_{(aq)}$ and Ln-EDTA are considered quantitatively by using the thermodynamic principles in couple with the improved RSPET equation. The previous thermodynamic studies of Ln-EDTA formation have overlooked the nephelauxetic effect relating to the hydration change of Ln-EDTA series, even though the hydration change of Ln-EDTA series itself had been pointed out.

10) Similar tetrad effects between ΔH_r and ΔS_r and their cancellation in ΔG_r

Similar large tetrad effects with convexity are seen in $\Delta H_r(hyc)$ and $\Delta S_r(hyc)$ data for the light Ln-EDTA formation of (20-2) (Fig. 5). The $\Delta\Delta H_r$ and $\Delta\Delta S_r$ values for the hydration change reaction (3') of the light Ln-EDTA (CN=9) to the heavy Ln-EDTA (CN=8) also show similar large tetrad effects with concavity (Fig. 6). Even though ΔH_r data obviously indicate tetrad effects, they are greatly diminished in ΔG_r ($=-2.303RT\log K$), because the series changes of ΔS_r involve the tetrad effects similar to those of ΔH_r . We define the proportionally constant of κ between $\Delta S_r(tetrad)$ and $\Delta H_r(tetrad)$ as

$$\kappa \equiv \Delta S_r(tetrad)/\Delta H_r(tetrad). \quad (27)$$

Therefore, eq. (25) is written in the following way:

$$\Delta G_r(\text{tetrad}) = \Delta H_r(\text{tetrad}) - T\Delta S_r(\text{tetrad}) = (1 - \kappa \cdot T) \Delta H_r(\text{tetrad}). \quad (28)$$

When $T = 298.15$ K and $\kappa \approx 1/T \approx 3 \times 10^{-3}$ (1/K), the series change of ΔG_r show no significant tetrad effect even when ΔH_r and ΔS_r data exhibit similar tetrad effects obviously. This situation is approximately realized in light Ln-EDTA complex formation. The proportionally constant of κ can be evaluated using C_1 and C_3 values for ΔS_r and ΔH_r :

$$\kappa(E^1) \equiv C_1(\Delta S_r)/C_1(\Delta H_r) \quad \text{and} \quad \kappa(E^3) \equiv C_3(\Delta S_r)/C_3(\Delta H_r). \quad (29).$$

Using C_1 and C_3 values for $\Delta S_r(\text{hyc})$ and $\Delta H_r(\text{hyc})$ for the reactions of (20-1) and (20-2) for the formation of two Ln-EDTA series (Table 4) and those for the $\Delta\Delta H_r$ and $\Delta\Delta S_r$ data for the hydration change reaction (3') (Table 5), we have calculated $\kappa(E^1)$ and $\kappa(E^3)$ values. They are summarized in Table 7.

In Table 7, the $\kappa(E^1)$ and $\kappa(E^3)$ for light Ln(III)-EDTA formation of (20-2) are respectively 2.9×10^{-3} and 2.5×10^{-3} (1/K). The large similar tetrad effects with convexity of $\Delta H_r(\text{hyc})$ and $\Delta S_r(\text{hyc})$ data for the light Ln-EDTA are cancelled in $\Delta G_r(\text{hyc})$ almost totally, because all the $\kappa(E^1)$ and $\kappa(E^3)$ values are fairly close to 3×10^{-3} (1/K). This explains the fairly smooth series variation of $\Delta G_r(\text{hyc})$ for light Ln-EDTA series in Figs. 4 and 5. In contrast, the series variation of $\Delta G_r(\text{hyc})$ for heavy Ln-EDTA series of (20-1) indicates a small concave tetrad effect in Fig. 5, because the small concave tetrad effect of $\Delta H_r(\text{hyc})$ for heavy Ln-EDTA series remains even in its $\Delta G_r(\text{hyc})$. This is the reason that the series change of $G_r(\text{hyc})$ for Ln-EDTA shows an asymmetrical tetrad-like variation across the entire Ln series (Figs. 4 and 5).

According to eq. (26), the insignificant $\Delta G_r(\text{tetrad})$ means either the situation of $\Delta H_r(\text{tetrad}) \approx 0$ or $(1-\kappa \cdot T) \cdot \Delta H_r(\text{tetrad}) \approx 0$ with $\Delta H_r(\text{tetrad}) \neq 0$. Therefore the apparently smooth series change of $\log K$ is the evidence for $\Delta H_r(\text{tetrad}) \approx 0$, only when the other case of $(1-\kappa \cdot T) \approx 0$ with $\Delta H_r(\text{tetrad}) \neq 0$ is rejected confidently. The apparently smooth series change of $\log K$ for light Ln-EDTA should not be raised as the evidence against the importance of the tetrad or nephelauxetic effect of Ln(III)-chelate complex formation, because their $\Delta H_r(\text{hyc})$ for $\Delta S_r(\text{hyc})$ values certainly indicate similar tetrad effects. Previous studies have overlooked the important facts of similar $\Delta H_r(\text{tetrad})$ and $\Delta S_r(\text{tetrad})$ and the resultant outcome of a diminished or cancelled $\Delta G_r(\text{tetrad})$.

11) “Gd-break” and subtle tetrad effect of $\log K(\text{Ln-EDTA})$

Here is discussed on the reason why the series change of $\log K(\text{Ln-EDTA})$ appears to show an apparent “Gd-break” even though the two series variations of $\Delta G_r(\text{hyc})$ for Ln-EDTA formation from $\text{Ln}^{3+}(\text{oct, aq})$ are intersecting at Eu not at Gd (Fig. 5). Figure 7 shows in an expanded scale the central part of the plots of $\Delta G_r(\text{hyc})$ for Ln-EDTA formation in Fig. 4. The series variations of $\Delta G_r(\text{hyc})$ for the formations of $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_2]^-_{(\text{aq})}$ and $[\text{Ln} \cdot \text{EDTA} \cdot (\text{H}_2\text{O})_3]^-_{(\text{aq})}$ of the reactions (20-1) and (20-2) are intersecting at Eu certainly. Note that the two series variations of $\Delta G_r(\text{hyc})$ are corresponding to (18-1) and (17-1), respectively, and that they are actually the same as (16-1) in the range that $\Delta \Delta G_r^0 > +11.4(\text{kJ/mol})$ or $\Delta \Delta G_r^0 < -11.4(\text{kJ/mol})$. But, the $\Delta G_r(\text{hyc})$ values for middle Ln(Sm~Tb)-EDTA with the condition that $-11.4(\text{kJ/mol}) \leq \Delta \Delta G_r^0 \leq +11.4(\text{kJ/mol})$ are expressed by (16-1) involving the term of

ΔG_{mixing} of (12). Therefore, the experimental value of $\Delta G_r(hyc)$ for Eu-EDTA and the calculated one by (16-1) are smaller than the intersection point value of $\Delta G_r(hyc)$ for $[Eu \cdot EDTA \cdot (H_2O)_2]_{(aq)}$ and $[Eu \cdot EDTA \cdot (H_2O)_3]_{(aq)}$ by $\Delta G_{mixing} \approx -RT \ln 2 \approx -1.7$ (kJ/mol).

In Fig. 7, the experimental values of $\Delta G_r(hyc)$ for the middle Ln-EDTA are connected by thick lines in order to indicate the negative contributions of ΔG_{mixing} for the middle Ln-EDTA with Ln=Sm, Eu, and Gd. Figure 7 shows that the calculated values (crosses) by eq. (16-1) are in good agreements with the experimental ones. The $\Delta G_r(hyc)$'s for Sm-, Eu-, and Gd-EDTA formations become smaller than those of the light or heavy Ln-EDTA series, because (16-1) involves the term of ΔG_{mixing} . Undoubtedly, the series variations of experimental and calculated $\Delta G_r(hyc)$ values show an apparent break at Gd as indicated by the thick lines of Fig. 7. This allows to point out a Gd-break, as far as only the data of ΔG_r or $\log K(\text{Ln-EDTA})$ are considered without paying attention to ΔH_r , ΔS_r and the spectroscopic ones mentioned above. As a matter of fact, the plots of Figs. 4, 5, and 7 illustrates that such an apparent Gd-break is caused by the fact that two series variations of $\Delta G_r(hyc)$ for the formations of $[Ln \cdot EDTA \cdot (H_2O)_2]_{(aq)}$ and $[Ln \cdot EDTA \cdot (H_2O)_3]_{(aq)}$ are intersecting at Eu, and by the term of ΔG_{mixing} in the equation (16-1).

On the other hand, the series change of $\Delta G_r(hyc)$ for light Ln-EDTA formation ($[Ln \cdot EDTA \cdot (H_2O)_3]_{(aq)}$) exhibits a faint convex tetrad effect (Figs. 5 and 7), which is the convex tetrad effect of $\Delta H_r(hyc)$ for $[Ln \cdot EDTA \cdot (H_2O)_3]_{(aq)}$ formation cancelled

by the similar convex tetrad effect of $T\Delta S_r(hyc)$ almost totally in $\Delta G_r(hyc)$. In contrast, a small concave tetrad effect is seen in the series variation of $\Delta G_r(hyc)$ for heavy Ln-EDTA formation ($[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$) (Figs. 5 and 7). Since $\Delta H_r(hyc)$ for the formation of $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$ exhibiting a small concave tetrad effect is combined with $\Delta S_r(hyc)$ with a faint convex tetrad effect, the resultant series change of $\Delta G_r(hyc)$ for heavy Ln-EDTA formation show a small concave tetrad effect (Figs. 5 and 7). Thus the tetrad effect variation of $\Delta G_r(hyc)$ is asymmetrical across the entire Ln series, even when the hydration change of light $Ln^{3+}(aq)$ series is corrected. As noted by Kawabe (2013a), the tetrad-like variation observed in the experimental $\log K(Ln-EDTA)$ is less symmetrical than the theoretical one expected from RSPET for Jørgensen's theory. This characteristics is explained naturally by the change of stable species of $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)}$ in light Ln into $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$ in the heavy Ln, and by the hydration change of $Ln^{3+}(aq)$ series occurring only in the light Ln.

Tetrad effect variations can also be said as “Gd-breaks”, because they exhibit breaks at Gd (Figs. 5 and 6). The tetrad effect, however, is given by the second and third terms of (21). In particular, the second term of $(9/13)n(S)C_1Z^*$ produces an octad-like variation with a break at Gd, unless C_1 in (21) is zero. Hence, the plots of Fig. 7 are clarifying the difference between the small octad-like variation with a subtle Gd-break and the apparent “Gd-break” caused by the hydration change of Ln-EDTA within the series. It is very important to distinguish the two types of Gd-breaks with the different origins: The first type is the octad-like variation involved in the lanthanide tetrad effect attributable to the Racah parameter differences between a pair of isomorphous Ln(III)

species, which relates to the importance of half-filled ($4f^7$) effect at Gd^{3+} as argued by Schwarzenbach and Gut (1956). The second type is a break of the series change properties due to a hydration change of Ln(III) complex species occurring in the vicinity of Gd position. In the case of the thermodynamic properties for Ln-EDTA formation, the observed apparent “Gd-break” is undoubtedly regarded as the second type, although the subtle Gd-break of the first type is recognized together (Figs. 5 and 7). No clear distinction between the two types of Gd-breaks may be one of the reasons that the long-lasting debates about the series variation of $\log K(\text{Ln-EDTA})$ have been made for more than thirty years.

Conclusions

The series change of $\log K(\text{Ln-EDTA})$ exhibits a Gd-break with a small tetrad-like variation has been a controversial subject, but the change of hydration states of Ln-EDTA across the series has been fairly well documented in the various studies by thermo-chemistry, UV-Vis spectroscopy, luminescence kinetics, lanthanide-induced ^{17}O shift in MNR, and X-ray or neutron structural analyses of hydrated Ln-EDTA salts for more than thirty years. The accumulated knowledge as to the hydration change of Ln-EDTA series has provided a sufficient situation for re-examining the long-lasting controversial subject on the unique characteristics of the series change of $\log K(\text{Ln-EDTA})$. Here is proposed a simple thermodynamic model from the following viewpoints: i) hydration changes in both Ln-EDTA and light $\text{Ln}^{3+}_{(\text{aq})}$ series, ii) the nephelauxetic effect correlating with the change of coordination number (CN) of Ln^{3+} ,

and iii) the improved RSPET equation for Jørgensen's theory applied to ΔH_r , ΔS_r and ΔG_r . The conclusions in this study are as follows:

- (1) Three water molecules possibly exist in the first-coordination spheres of light Ln(La~Nd)-EDTA as $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)}$, but two water molecules do in those of heavy Ln(Dy~Lu)-EDTA of $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$. The coordination numbers (CN) for Ln^{3+} in the two Ln-EDTA series are 9 and 8, respectively. Each middle Ln(Sm~Tb)-EDTA is a mixture of the two distinct hydrate species, and their abundances are given by the equilibrium of $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)} = [Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)} + H_2O_{(l)}$. The coordination numbers of Ln^{3+} are possibly comparable with those in crystalline salts of $M[Ln(III) \cdot EDTA \cdot (H_2O)_n] \cdot mH_2O$.
- (2) When the hydration changes in both Ln-EDTA and light $Ln^{3+}_{(aq)}$ series are corrected, the series variations of ΔH_r , ΔS_r and ΔG_r for Ln-EDTA formation can be described by the improved equation of RSPET. The thermodynamic parameters for the formations of two Ln-EDTA series from octahydrate $Ln^{3+}_{(aq)}$ have been evaluated. Our model gives the hydration numbers compatible with the studies of luminescence decay constants for the middle Ln-EDTA including Eu and Tb members within their uncertainties.
- (3) The nephelauxetic effect correlating with the CN change of Ln^{3+} is clearly seen in ΔH_r data for the three reactions: (a) $[Ln \cdot EDTA \cdot (H_2O)_3]^-_{(aq)}$ formation from $Ln^{3+}_{(octa. aq)}$, (b) $[Ln \cdot EDTA \cdot (H_2O)_2]^-_{(aq)}$ formation from $Ln^{3+}_{(octa. aq)}$, and (c) the hydration change reaction given as (b) – (a). The CN changes of Ln^{3+} (ΔCN) in (a), (b), and (c) are +1, 0, and –1, respectively. The relative Racah E^1 parameter values

for Nd^{3+} , $\Delta E^1(\text{Nd}^{3+})$, evaluated from the tetrad effects of ΔH_r for (a), (b), and (c), are $+39 \text{ cm}^{-1}$, -19 cm^{-1} , and -58 cm^{-1} , respectively. $\Delta E^3(\text{Nd}^{3+})$ is also correlating with ΔCN .

- (4) The ΔH_r values for the reaction (a) with $\Delta \text{CN}=+1$ show a large convex tetrad effect, and the ΔS_r values also exhibit a similar tetrad effect. Therefore, the two tetrad effects of ΔH_r and $T\Delta S_r$ are cancelled in ΔG_r almost totally. This makes series the variation of $\log K(\text{Ln-EDTA})$ relatively smooth in the light Ln, but it does the variation asymmetrical between light and heavy Ln series.
- (5) The apparent Gd-break of $\log K(\text{Ln-EDTA})$ with a subtle tetrad-like variation is explained by the hydration changes of middle Ln-EDTA series, the nephelauxetic effect correlating with the CN change of Ln^{3+} , and hydration change of light $\text{Ln}^{3+}_{(\text{aq})}$ series. These make the series variation of $\log K(\text{Ln-EDTA})$ somewhat different from the other (1:1) Ln-chelate complexes.
- (6) The thermodynamic data for Ln-EDTA formation provide a good example illustrating that not only the hydration changes of the Ln(III) complex series but also tetrad and nephelauxetic effects are important in Ln(III) complexation. The thermodynamic principles coupled with the improved RSPET equation for Jørgensen's theory allow to make the quantitative analysis of ΔG_r , ΔH_r , and ΔS_r data for aqueous Ln(III) complex formation in reference to available lines of spectroscopic evidence for hydration states Ln(III)-complexes by UV-Vis, luminescence, and water ^{17}O MNR methods.

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