

Thermodynamic parameters for aqueous lanthanide(III)-DTPA complex formations:

Convex tetrad effects of ΔH_r and ΔS_r cancelled in ΔG_r almost totally

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Abstract

Thermochemical data for lanthanide(III)-DTPA (diethylenetriaminepentaacetate) complex formations at 27°C and I=0.1 M, have been examined from Jørgensen's theory (RSPET) and the hydration change in light $\text{Ln}^{3+}_{(\text{aq})}$ series relative to the octahydrate heavy $\text{Ln}^{3+}_{(\text{aq})}$. The ΔH_r , ΔS_r and ΔG_r data corrected for the hydration change of light $\text{Ln}^{3+}_{(\text{aq})}$, can be regressed by the improved RSPET equation, with exception of ΔG_r for La-DTPA and ΔH_r for Lu-DTPA. The exceptional data have been corrected according to the RSPET equation, along with small experimental biases in ΔH_r for Dy-DTPA and ΔG_r for Er-DTPA. Racah (E^1 and E^3) parameters of Ln-DTPA are greater than those of octahydrate $\text{Ln}^{3+}_{(\text{aq})}$: $\Delta E^1=+(17\pm 7) \text{ cm}^{-1}$ and $\Delta E^3=+(10\pm 2) \text{ cm}^{-1}$ for Ln=Nd. The corrected ΔH_r and ΔS_r data show similar convex tetrad effects, whereas the ΔG_r data exhibit a fairly smooth variation. The tetrad effects of ΔH_r and ΔS_r are positively correlated: $\Delta S_r(\text{tetrad}) \approx \kappa \cdot \Delta H_r(\text{tetrad})$ with $\kappa(E^1) = (2.9 \pm 1.5) \times 10^{-3} (1/K)$ and $\kappa(E^3) = (2.4 \pm 0.7) \times 10^{-3} (1/K)$. The tetrad effect of ΔG_r is given as $\Delta G_r(\text{tetrad}) = \Delta H_r(\text{tetrad}) - T\Delta S_r(\text{tetrad}) \approx (1 - \kappa \cdot T)\Delta H_r(\text{tetrad})$. At $T \approx 300 \text{ K}$, $\Delta H_r(\text{tetrad})$ is cancelled by $T\Delta S_r(\text{tetrad})$ in $\Delta G_r(\text{tetrad})$ almost totally. This is the reason why the experimental values of $\log K(\text{Ln-DTPA}) = -\Delta G_r/(2.303RT)$ do not exhibit an obvious tetrad effect.

Combining the Ln-DTPA formation with the solution of isomorphous Ln(III) ethylsulphate nonahydrate ($\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$) eliminates $\text{Ln}^{3+}_{(\text{aq})}$, and gives the following reaction that $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}_{(\text{c})} + \text{DTPA}^{5-}_{(\text{aq})} = [\text{Ln} - \text{DTPA}]^{2-}_{(\text{aq})} + 3\text{ES}^{-}_{(\text{aq})} + 9\text{H}_2\text{O}_{(\text{l})}$. Thermochemical data for this reaction are useful to see structural changes and Racah parameters of Ln-DTPA relative to $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$. They show smooth variations with

minor tetrad effects compatible with RSPET. Racah (E^1 and E^3) parameters of Ln-DTPA are fairly comparable with those of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$, suggesting that a nine-fold coordination of Ln^{3+} in Ln-DTPA with the octadentate DTPA ligands plus one water molecule is analogous to $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$. This is compatible with the results by the fluorescence lifetime studies of Ln-DTPA (Ln=Eu, Tb, Dy and Yb), XAFS study of Gd-DTPA, and multinuclear NMR study of Ln-DTPA series. Since the NMR study of the lanthanide-induced ^{13}C and water ^{17}O shifts suggests an isostructural inner coordination of Ln^{3+} across the Ln-DTPA series, the exceptional thermochemical data for La-DTPA and Lu-DTPA are possibly attributable to experimental errors. The thermochemical data for Ln-DTPA complex formation provide such an example that shows similar convex tetrad effects of ΔH_r and ΔS_r cancelled in ΔG_r almost totally. Its implications to REE solution chemistry and geochemistry have been discussed.

Introduction

The lanthanide tetrad effect (Peppard et al., 1969) or double-double effect (Fidelis and Mioduski, 1981) is sometimes observed, when thermochemical data (ΔG_r^0 and ΔH_r^0) for low-temperature reactions between pairs of lanthanide(III) compound or complex series are plotted against the number of 4f electrons (q) in the electronic configuration of $[\text{Xe}](4f^q)$ for Ln^{3+} . The number of 4f electrons (q) is given by $q=Z-57$, where Z is the atomic number of Ln. Jørgensen's refined spin-pairing energy theory (RSPET) explains the lanthanide tetrad effect: it is the thermochemical consequence of nephelauxetic effect known as the spectroscopic observations of small systematic differences in Racah (E^1 and E^3) parameters for Ln^{3+} with $[\text{Xe}](4f)^q$ between a pair of Ln(III) compound or complex series (Jørgensen, 1970, 1971 and 1979; Nugent, 1970; Reisfeld and Jørgensen, 1977). Jørgensen's RSPET has been improved and applied to thermodynamic quantities successfully (Kawabe 1992 and 1999a; Kawabe and Masuda, 2001).

Wood (1990), referring to the reported tetrad, double-double, or nephelauxetic effect of aqueous Ln(III) complex formations, wrote that "this effect is nevertheless difficult to detect for most geologically important ligands at 25°C and probably is of little consequence to the behavior of REE in low-temperature geological fluids." Byrne and Sholkovitz (1996) also presented a skeptical comment on the tetrad effects of Ln(III) complexing behavior in aquatic marine environments. However, Kawabe(1999b) and Ohta and Kawabe (2000a, b) showed that the series variations of $\log\beta(\text{LnCO}_3^+, \text{aq})$ and $\log\beta(\text{Ln}(\text{CO}_3)_2^-, \text{aq})$ indicate convex tetrad effects clearly, when the hydration change of light $\text{Ln}^{3+}_{(\text{aq})}$ relative to heavy $\text{Ln}^{3+}_{(\text{aq})}$ (Kawabe, 1999a) and small irregularities of

$\log\beta(\text{Ln}(\text{CO}_3)_2^-, \text{aq})$ with $\text{Ln}=\text{La}, \text{Ce},$ and Pr are corrected. The logarithmic stability constants ($\log\beta$) or complex formation constants ($\log K$) for $\text{LnCO}_3^+_{(\text{aq})}$ and $\text{Ln}(\text{CO}_3)_2^-_{(\text{aq})}$ are important for REE geochemistry of aqueous marine environments, because total $\text{Ln}(\text{III})$ dissolved in normal seawater is the sum of $\text{LnCO}_3^+_{(\text{aq})}$ and $\text{Ln}(\text{CO}_3)_2^-_{(\text{aq})}$.

On the other hand, characteristic series changes of $\log K$ for aqueous $\text{Ln}(\text{III})$ complex formations have been known in many $\text{Ln}(\text{III})$ -chelate complexes (Moeller et al., 1965; Geier and Karlen, 1971; Moeller, 1973; Choppin et al., 1977; Thompson, 1979; Sinha, 1983; Suzuki, 1999). The series variations of $\log K$ for selected (1:1) $\text{Ln}(\text{III})$ chelate complexes including those with DTPA, EDTA, NTA, and dipicolinate are shown in Fig. 1. The series change patterns of $\log K$ are fairly different from one $\text{Ln}(\text{III})$ complex series to another. The Ln -EDTA series suggests a tetrad-like variation and Gd-break, but Ln -NTA and Ln -dipicolinate series appear to show sigmoidal curves without marked tetrad-like variations. The Ln -DTPA series also exhibits a smoothly curved trend, and it seems difficult to see an obvious tetrad-like variation in this scale of Fig. 1. The situation of Fig. 1 might be the circumstantial evidence against the tetrad effect and Gd-break for the majority in REE solution chemistry and geochemistry. This seems to be the ground for the negative and skeptical comments concerning the tetrad effect by Wood (1990) and Byrne and Sholkovitz (1996).

However, in this paper, we will demonstrate that the previous studies of $\text{Ln}(\text{III})$ solution chemistry have overlooked the important experimental evidence for the tetrad effect being illustrated by the thermodynamic data for aqueous Ln -DTPA complex formations: ΔH_r and ΔS_r for the Ln -DTPA formations involve convex tetrad effects obviously, and they

are compatible with the improved RSPET equation (Kawabe, 1992 and 1999a). This can be seen only when they are corrected for the hydration change in light $\text{Ln}^{3+}(\text{aq})$ and irregularities accompanied with data for La-DTPA and Lu-DTPA formations. The smooth variation of $\log K$ for Ln-DTPA series (Fig. 1) is the result of cancellation of convex tetrad effects of ΔH_r and $T\Delta S_r$ in $\Delta G_r = -2.303RT\log K$ almost totally. The smoothly curved variation of $\log K$ for Ln-DTPA series is not the immediate evidence against the tetrad effect, but this is an example illustrating the important thermodynamic property of the tetrad effect in aqueous Ln(III) complex formations.

Results and Discussion

1) Tetrad effects in ΔH_r and ΔS_r for Ln(III)-DTPA formation cancelled in ΔG_r

The series variations of experimental ΔH_r , ΔS_r and ΔG_r for the aqueous Ln(III)-DTPA (diethylenetriaminepentaacetate) complex formations at 27°C and an ionic strength of 0.1 M (Carson et al., 1968) are shown in Fig. 2. The reported data are cited in Table 1. Carson et al. (1968) accepted the $\log K$ data for Ln-DTPA formation at 25°C reported by Moeller's group (Moeller et al., 1965), and they calculated $\Delta S_r = (\Delta H_r - \Delta G_r)/T$ by combining their ΔH_r data and the $\log K$ data corrected to ΔG_r values at 27°C. Although Carson et al. (1968) listed their ΔH_r value for Ce-DTPA, they did not list ΔG_r and ΔS_r values for Ce-DTPA formation, even though Moeller's group reported all the $\log K$ values including that for Ce-DTPA formation. We have corrected the $\log K$ value (=20.5) for Ce(III)-DTPA formation at 25°C (Moeller et al., 1965) to the ΔG_r value at 27°C, and calculated the ΔS_r value using the ΔH_r and ΔG_r data for Ce-DTPA

formation. Choppin et al. (1977) have reported ΔH_r , ΔS_r and ΔG_r data at 25°C and I=0.5 M for Ln(III)-DTPA formations, together with those for several Ln(III)-chelate complex series. Their data, however, appear to have significant salt effects due to the condition of I=0.5 relative to those results at I=0.1 M by Moeller et al. (1965) and Carson et al. (1968). Therefore, the thermochemical data by Choppin et al. (1977) will not be discussed here.

DTPA is a typical octadentate ligand having eight electron donor groups in aqueous solutions. They are three nitrogen atoms and five carboxylate oxygen atoms of DTPA. The Gd(III)-DTPA complex and the other Gd(III) complexes with polyamino polycarboxylate ligands are currently used clinically as magnetic resonance imaging (MRI) contrast agents. Hence a considerable attention has been paid to the static and dynamic structural properties of aqueous Gd-DTPA complex and its analogues in recent years (Choppin and Schaab, 1996; Bénazeth et al., 1998; Balogh et al., 2006). Some geochemists (Bau and Dulski, 1996; Möller et al., 2000), on the other hand, concerned with the Gd pollution in natural water systems by the intensive clinical use of aqueous Gd(III) chelate complexes as MRI contrast agents.

The complex formation reaction of DTPA with $\text{Ln}^{3+}_{(aq)}$ is written as follows:



where water molecules ligating with each species are not expressed explicitly. When the thermodynamic effects of hydration changes in light $\text{Ln}^{3+}_{(aq)}$ relative to heavy $\text{Ln}^{3+}_{(aq)}$ series (Kawabe, 1999a) are corrected (Fig. 2), the experimental data of ΔH_r , ΔS_r , and ΔG_r become more regular and monotonous than the original ones. Although the data for

hydration changes in light $\text{Ln}^{3+}(\text{aq})$ are at 25°C (Kawabe, 1999a), the small temperature difference of 2°C is neglected here. The ΔH_r and ΔS_r data for Lu-DTPA formation and the ΔG_r and ΔS_r data for La-DTPA formation, however, are apparently deviating from the monotonous trends by the others. The improved RSPET equation (Kawabe, 1992) has been fitted successfully to the data sets of ΔH_r , ΔS_r and ΔG_r corrected for hydration changes of light $\text{Ln}^{3+}(\text{aq})$ relative to the octahydrate heavy $\text{Ln}^{3+}(\text{aq})$ (Fig. 3), except for the apparently irregular data for La-DTPA and Lu-DTPA formations. The RSPET equation is given in the simple form,

$$\Delta Y(q) = [(a + bq) qZ^* + c] + (9/13)n(S)C_1Z^* + m(L)C_3Z^*, \quad (2)$$

where $\Delta Y(q)$ denotes the corrected data of ΔH_r , ΔS_r and ΔG_r , and q denotes the number of 4f electrons in the electronic configuration $[\text{Xe}](4f)^q$ for Ln^{3+} . The effective nuclear charge ($Z^* = Z - S_{4f}$) for 4f electrons of Ln^{3+} is given by $(q+25)$. The first term in (2) is for the smooth variation component of $\Delta Y(q)$. The second and third terms in (2) 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 coefficients of $n(S)$ and $m(L)$ are the theoretical constant coefficients associated with the energy contributions by Racah E^1 and E^3 parameters, in which S and L denote the total spin and total 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 that can be determined in the least-squares fitting.

When the ΔH_r data are input into $\Delta Y(q)$ of (2), the Racah E^1 and E^3 parameters of Ln(III)-DTPA relative to octahydrate $\text{Ln}^{3+}(\text{aq})$ are given as $\Delta E^1 = C_1(q+25)$ and

$\Delta E^3=C_3(q+25)$. The observed convex tetrad effect in ΔH_r in Fig. 3 means that the Racah (E^1 and E^3) parameters of Ln^{3+} in Ln(III)-DTPA complex series are fairly greater than those in octahydrate $\text{Ln}^{3+}_{(\text{aq})}$ series. The differences in E^1 and E^3 parameters between Nd(III)-DTPA and octahydrate $\text{Nd}^{3+}_{(\text{aq})}$ can be calculated from C_1 and C_3 values (Table 2-A) and $q=3$ for the Nd^{3+} pair:

$$\Delta E^1(\text{Nd})=+(17\pm 7) \text{ cm}^{-1} \quad \text{and} \quad \Delta E^3(\text{Nd})=+(10\pm 1) \text{ cm}^{-1}. \quad (3)$$

The experimental ΔH_r data for Dy- and Lu-DTPA formations deviate from the regressed values by -1.5 kJ/mol and +4 kJ/mol, respectively. In particular, the experimental ΔH_r and ΔS_r data for Lu-DTPA formation are much greater than those for Yb and Tm members. In view of the reported experimental error of ± 1.3 kJ/mol for ΔH_r data (Carson et al., 1968), it seems difficult to account for the deviation of +4 kJ/mol of $\Delta H_r(\text{Lu-DTPA})$ by the small experimental error. There might be such a possibility that the anomalies for Lu-DTPA formation represent a certain structural change of Lu-DTPA relative to the others. All the ΔS_r values are calculated as $\Delta S_r = (\Delta H_r - \Delta G_r)/T$ using experimental data of ΔH_r and ΔG_r . In order to eliminate the anomalies for Lu-DTPA irrespective of their origins of the experimental error or the structural change, we have made the empirical corrections of -4.0 kJ/mol for ΔH_r , -11 J/mol/K for ΔS_r , and -0.7 kJ/mol for ΔG_r , in which the relation that $\Delta G_r = \Delta H_r - T\Delta S_r$ is taken into account. In the case of ΔH_r for Dy-DTPA, the deviation of -1.5 kJ/mol is comparable with the experimental error of ± 1.3 kJ/mol for each complex (Carson et al., 1968), and this may be due to an experimental error in the calorimetric measurement. Hence we have made the corrections of +1.5 kJ/mol for ΔH_r , +3 J/mol/K for ΔS_r , and +0.6 kJ/mol for ΔG_r . Our

corrections for the data for Lu-DTPA and Dy-DTPA are listed in Table 1. The results of (3) have been obtained using the data with the empirical corrections for ΔH_r data of Lu-DTPA and Dy-DTPA.

2) Important thermodynamic relation that $\Delta G_r(\text{tetrad}) = \Delta H_r(\text{tetrad}) - T\Delta S_r(\text{tetrad})$

When the ΔH_r data are fitted to (2), the resultant parameter values of C_1 and C_3 directly correspond to the differences of Racah (E^1 and E^3) parameters for Ln^{3+} between the pair of Ln(III) complexes. However, such meanings of C_1 and C_3 are lost, when eq. (2) is applied to ΔG_r or ΔS_r data. Our purpose of applying the RSPET equation (2) to ΔG_r or ΔS_r data is to show that the smooth and tetrad effect components of the series variations of ΔG_r or ΔS_r can be evaluated practically, and that the RSPET equation (2) is applicable to the thermodynamic data other than ΔH_r for aqueous Ln(III)-DTPA complex formations (Kawabe, 1999a,b). If we make sure that ΔH_r , ΔG_r and ΔS_r data can be regressed by the RSPET equation (2), it follows that the relation that $\Delta G_r = \Delta H_r - T\Delta S_r$ with respect to the tetrad effect component holds true, because the tetrad effect component in (2) is an additive term and the relation that $\Delta G_r = \Delta H_r - T\Delta S_r$ is a linear relationship with a constant factor of T.

The data of ΔG_r and ΔS_r can be fitted to the equation (2) successfully like the case of the ΔH_r data, but it is evident that additional corrections are necessary for the ΔG_r and ΔS_r data of La-DTPA (-4.2 kJ/mol and +16 J/mol/K, respectively). It is not certain whether the discrepancies in ΔG_r and ΔS_r for La-DTPA formation are due to an experimental error in $\Delta G_r = -RT \ln K$ or a structural change of La-DTPA, but we have

made empirical corrections for them, like those data for Lu-DTPA formation. According to the fluorescence lifetime studies of Ln-DTPA (Ln=Eu, Tb, Dy and Yb), the XAFS study of Gd-DTPA, and the multinuclear NMR study of Ln-DTPA series as discussed in the later subsection 4), one water molecule is present in the first-coordination spheres of each member of Ln-DPTA across the entire series. In particular, the multinuclear NMR study (Peters, 1988) suggests no significant structural changes in the first coordination sphere of Ln-DTPA series across the series, hence our empirical corrections for the irregular thermochemical data for La and Lu members could be justified as will be discussed in 4).

In addition, the ΔS_r value for Er-DTPA is deviating from the regressed one by -4 J/mol/K, while its ΔH_r value shows no such a significant deviation (Fig. 3). All the ΔS_r values are the calculated ones according to $\Delta S_r = (\Delta H_r - \Delta G_r)/T$. The negative deviation of the ΔS_r value for Er-DTPA is possibly caused by a positive small error of the experimental ΔG_r value. We have corrected the ΔS_r and ΔG_r values for Er-DTPA by $+4$ J/mol/K and -1.2 kJ/mol, respectively. All the corrections by us are listed in Table 1.

The ΔH_r , ΔS_r and ΔG_r data in Fig. 3 become compatible with the RSPET equation (2), when they are corrected for (i) hydration changes of light $\text{Ln}^{3+}_{(\text{aq})}$, (ii) apparently irregular data for La and Lu members of the Ln(III)-DTPA series, and (iii) possible small experimental errors of ΔH_r and ΔG_r for Dy-DTPA and Er-DTPA formations. Since the corrected data satisfy the relation that $\Delta G_r = \Delta H_r - T\Delta S_r$, the analogous equation with respect to the tetrad effect also holds true:

$$\Delta G_r(\text{tetrad}) = \Delta H_r(\text{tetrad}) - T\Delta S_r(\text{tetrad}), \quad (4)$$

where $\Delta G_r(\text{tetrad})$, $\Delta H_r(\text{tetrad})$, and $\Delta S_r(\text{tetrad})$ denote the tetrad effect components of the

respective thermodynamic quantities that can be expressed by the sum of the second and third terms in (2). The C_1 and C_3 parameters in (2) represent the sizes and polarities of the octad- and tetrad-like variations, respectively. Table 2-A summarizes the C_1 and C_3 parameter values determined in the least-squares fittings shown in Fig. 3. The C_1 and C_3 values in the fitting of ΔG_r data are compared with the calculated C_1 and C_3 parameter values from those in the fittings of the ΔH_r and ΔS_r data (Table 2-A). They are in a good agreement, indicating that our results of least-squares fittings for ΔH_r , ΔS_r and ΔG_r are satisfying the relation (4) within fitting errors.

The results of Fig. 3 and Table 2-A are illustrating that $\Delta G_r(tetrad)$ is very small because similar convex tetrad effects of $\Delta H_r(tetrad)$ and $T\Delta S_r(tetrad)$ are cancelled in $\Delta G_r(tetrad)$ almost totally. This is a very interesting and important result for the thermochemical parameters for Ln-DTPA complex formations, and for our understanding of $\Delta G_r(tetrad)$ in general. Since $\Delta H_r(tetrad)$ and $\Delta S_r(tetrad)$ in Fig. 3 are mutually similar, they can be written approximately in the form,

$$\Delta S_r(tetrad) \approx \kappa \cdot \Delta H_r(tetrad), \quad (5)$$

where κ is a proportionality constant evaluated from the C_1 or C_3 parameter values listed in Table 2-A:

$$\kappa(E^1) \equiv C_1(\Delta S_r)/C_1(\Delta H_r) = (2.9 \pm 1.5) \times 10^{-3} (1/K), \quad (6-1)$$

$$\kappa(E^3) \equiv C_3(\Delta S_r)/C_3(\Delta H_r) = (2.4 \pm 0.7) \times 10^{-3} (1/K). \quad (6-2)$$

Using (5), we can rewrite (4) in the form,

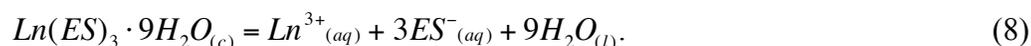
$$\Delta G_r(tetrad) = \Delta H_r(tetrad) - T\Delta S_r(tetrad) \approx (1 - \kappa \cdot T)\Delta H_r(tetrad). \quad (7)$$

In the case of Ln-DTPA formations at T=300 K, it follows that $[1 - \kappa(E^1) \cdot T] \approx 0.1$ and

$[1 - \kappa(E^3) \cdot T] \approx 0.3$. The octad effect in $\Delta H_r(tetrad)$ is almost the same as that in $T\Delta S_r(tetrad)$, although 30 % of the intrinsic tetrad effect in $\Delta H_r(tetrad)$ remain in $\Delta G_r(tetrad)$. This is the reason that the series variation of logarithmic complex formation constants for Ln-DTPA appears fairly smooth with a faint tetrad effect (Fig. 1). Hence the apparently smooth variation of $\log K = -\Delta G_r / (2.303RT)$ is not the evidence against the tetrad effect, because obvious convex tetrad effects are involved in ΔH_r and ΔS_r (Fig. 3). This point has been overlooked in the previous studies.

3) Ln(III)-DTPA complex formation combined with solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$

The data of ΔH_r , ΔS_r and ΔG_r corrected for the hydration change of light $\text{Ln}^{3+}_{(aq)}$ were used in the least-squares fittings to the RSPET equation (2), but they involve two types of our corrections for (i) apparently irregular data for La-DTPA and Lu-DTPA and (ii) possible experimental errors for Dy and Er members. In order to inspect further possible structural changes in the Ln-DTPA series and experimental errors, we have combined the Ln-DTPA formation with the solution reaction of the fully isomorphous Ln(III) ethylsulphate nonahydrate series ($\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$) with CN (coordination number) = 9 for all Ln^{3+} ions (Staveley et al., 1966 and 1968; Kawabe, 1999a). The solution reaction of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ is written as



The sum of (1) and (8) gives the following reaction without the involvement of $\text{Ln}^{3+}_{(aq)}$:



Because the hydrate crystal series of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ are isomorphous across the entire Ln

series, structural changes within the Ln-DTPA series, if present, can be seen as irregularities in the series variations of ΔH_r , ΔS_r , and ΔG_r for (9). Also they may show anomalies by experimental errors of thermodynamic data for Ln-DTPA formations and the tetrad effect due to different Racah parameters between Ln-DTPA and Ln(ES)₃·9H₂O series as well. The thermodynamic data for solution of Ln(ES)₃·9H₂O series are at 25°C (Kawabe, 1999a), whereas those data for Ln-DTPA formations are at 27°C. We regard possible effects due to the small temperature difference of 2°C are negligible.

The series variations of ΔH_r , ΔS_r , and ΔG_r for (9) are shown in Fig. 4, in which their fittings to the RSPET equation (2) by the method of least squares are also shown. The original data points of Lu and Dy in ΔH_r are showing deviations from the fitted curve as in Fig.3. The data points of La, Dy, Er and Lu in ΔS_r and the point of La in ΔG_r are also incompatible with the regressed curves having small tetrad effects. This situation is the same as what is seen in the plots of Fig. 3. Hence, it could be concluded from the thermochemical data that the inner coordination spheres of Ln³⁺ of Ln-DTPA complexes are isostructural except for the two end members of La-DTPA and Lu-DTPA. Whether or not La-DTPA and Lu-DTPA are isostructural together with the other members, cannot be determined by the present thermochemical data alone. In this context, the multinuclear NMR study by Peters (1988) is important: the MNR study strongly suggests that one water molecule is present in the first coordination spheres of all members of Ln-DTPA without changing the average structures of inner coordination spheres. This is compatible with the plots of the thermodynamic data for (9) in Fig. 4. Our empirical corrections to the thermodynamic data for Ln-DTPA formations with Ln=La, Dy, Er and Lu shown in Fig. 3,

could be acceptable as will be discussed in 4).

The C_1 and C_3 parameter values of the RSPET equation (2) for each set of thermodynamic data for (9) are summarized in Table 2-B, where it is shown that the relation (4) is valid for the reaction (9). The values of $\Delta H_r(tetrad)$ and $T\Delta S_r(tetrad)$ for the reactions (9) explain the small concave tetrad effect in ΔG_r for (9). The series variation of ΔH_r indicates a small convex tetrad effect with respect to Racah E^3 parameter: the E^3 parameters of Ln^{3+} in Ln -DTPA(aq) are slightly larger than those in $Ln(ES)_3 \cdot 9H_2O$ series, whereas the subtle concave octad effect is suggesting that Ln -DTPA(aq) have the Racah E^1 parameters a little smaller than $Ln(ES)_3 \cdot 9H_2O$ series. The evaluated E^1 and E^3 parameters of Nd-DTPA relative to $Nd(ES)_3 \cdot 9H_2O$ are as follows:

$$\Delta E^1(Nd) = -(6 \pm 6) \text{ cm}^{-1} \quad \text{and} \quad \Delta E^3(Nd) = +(4 \pm 2) \text{ cm}^{-1}. \quad (10)$$

When the Racah parameter differences between Nd-DTPA and octahydrate $Nd^{3+}_{(aq)}$ of (3) are subtracted by those between Nd-DTPA and $Nd(ES)_3 \cdot 9H_2O$ of (10), they give the Racah parameters of $Nd(ES)_3 \cdot 9H_2O$ relative to octahydrate $Nd^{3+}_{(aq)}$:

$$\Delta E^1(Nd) = +(23 \pm 9) \text{ cm}^{-1} \quad \text{and} \quad \Delta E^3(Nd) = +(6 \pm 2) \text{ cm}^{-1}. \quad (11)$$

Kawabe (1999a) reported the relative Racah (E^1 and E^3) parameter values by fitting the ΔH_r data for solution of $Ln(ES)_3 \cdot 9H_2O$ to the RSPET equation (2), in which the Racah parameters of $Nd(ES)_3 \cdot 9H_2O$ relative to octahydrate $Nd^{3+}_{(aq)}$ were evaluated as follows:

$$\Delta E^1(Nd) = +(23 \pm 6) \text{ cm}^{-1} \quad \text{and} \quad \Delta E^3(Nd) = +(4.9 \pm 1.8) \text{ cm}^{-1}. \quad (12)$$

The indirect calculations of (11) are in excellent agreements with the direct estimates of (12), indicating that the three sets of (3), (10), and (12) for Racah parameter differences are consistent among Ln -DTPA, octahydrate $Ln^{3+}_{(aq)}$, and $Ln(ES)_3 \cdot 9H_2O$ series.

The plots of Fig. 4 and the Racah parameter relation (10) suggest that the coordination number of Ln^{3+} in Ln-DTPA complex series except Ln=La and Lu, is nine like the Ln(III) ethylsulphate nonahydrate series. The nine fold-coordination differs from the number of eight electron donor groups of DTPA, indicating that one water molecule is involved in the inner coordination sphere of Ln^{3+} of Ln-DTPA in solution. This inference from the plots of Fig. 4 will be compared with the reported studies as to the coordination states of Ln^{3+} in aqueous Ln-DTPA complexes by variously different techniques in the next.

4) Coordination of Ln^{3+} in Ln-DTPA inferred by different techniques

The fluorescence kinetic measurements of aqueous Eu-DTPA, Tb-DTPA, and Yb-DTPA (Rizkalla and Choppin, 1991; Brittain et al, 1992; Beeby et al., 1999; Supkowski and Horrocks, 2002) show that one water molecule exists in the first coordination sphere, namely, the nine-fold coordination of Ln^{3+} in Ln-DTPA with Ln=Eu, Tb and Yb. Kimura and Kato (1998) applied the luminescence technique not only to the complexes of Eu(III) and Tb(III) but also to those of Sm (III) and Dy (III). They reported that the numbers of water molecules in the inner spheres of Ln-DTPA series are 2.4 ± 0.3 for Sm-DTPA, 1.1 ± 0.3 for Eu-DTPA, 1.1 ± 0.3 for Tb-DTPA, and 1.5 ± 0.3 for Dy-DTPA. Although two water molecules or more are suggested for Sm-DTPA, the presence of one water molecule is supported in the other three Ln members, which is consistent with the fluorescence decay constant studies cited as above.

Bénazeth et al. (1998), on the basis of XAFS study of Gd-DTPA complex in solution, showed that Gd^{3+} is coordinated by three nitrogen atoms and five carbonyl oxygen atoms of

DTPA⁵⁻ plus a water molecule. This supports our inference that one water molecule is involved in the first coordination sphere of Ln³⁺ of each member of Ln-DTPA series. Peters (1988) reported ¹H, ¹³C, ¹⁷O, and ⁶Li NMR shifts and relaxation measurements for Ln(III)-DTPA series in solution, and concluded that in all members of Ln(III)-DTPA there exists one water molecule in the first coordination sphere. Peters (1988) carried out the analyses of the lanthanide-induced shifts (LIS) of ¹³C NMR and water ¹⁷O NMR in the inner coordination spheres of Ln-DTPA series, and suggested that the first coordination sphere of Ln³⁺ with DTPA⁵⁻ plus one water molecule is isostructural across the entire Ln-DTPA series.

In the crystal structures of hydrate salts of Ln-DTPA complexes, (NH₄)₂[Ln-DTPA]·4H₂O with Ln=Dy, Ho, Er, and Yb and other types of salts (Inomata et al., 2003 and references therein), two different coordination spheres of Ln³⁺ with CN=9 have been reported: one is a capped square antiprism (CSAP) with three N and five O of DTPA⁵⁻ and one capping water molecule. The other is a tricapped trigonal prism (TTP) with three N and five O of DTPA⁵⁻ and one carboxylato O from an adjacent complex ion, which means a dimer-like structure. Wang et al. (2002) also reported the dimer-like structure with CN=9 in (NH₄)₄[Yb₂(DTPA)₂]·9H₂O. The CSAP structure of the nine-coordination of Ln³⁺ in crystalline hydrate salts of mononuclear Ln-DTPA complexes, may be comparable with those in aqueous Ln-DTPA complexes of our interest.

Thus the different techniques indicate or support the nine-coordinated Ln³⁺ of inner coordination spheres of aqueous Ln-DTPA complex series with DTPA⁵⁻ plus one water molecule. This is compatible with our interpretation of the thermochemical data by the

improved RSPET equation (Figs. 3 and 4). The nine fold coordination of Ln^{3+} in Ln-DTPA is significantly related to our results of (3), (10) and (11) as to the nephelauxetic effects: the Racah (E^1 and E^3) parameter differences of (3) for the pair of Nd-DTPA(aq) with CN=9 and octahydrate Nd^{3+} (aq) with CN=8 are definitely positive. This is comparable with the nephelauxetic effects of (11) for the pair of $\text{Nd}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c})$ and octahydrate Nd^{3+} (aq). By contrast, the differences of (10) for the pair of Ln-DTPA(aq) and $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c})$ both of which have Ln^{3+} with CN=9, are much smaller and closer to zero. The increased average Ln(III)-ligand distances with CN = 9 relative to those with CN=8 give rise to the positive differences in Racah (E^1 and E^3) parameters like (3) and (11). This means the increased Racah parameters corresponding to the increased average Ln(III)-ligand distances. In particular, the case of (11) represents the nephelauxetic effect due to the change of average Ln(III)-ligand distances, since the ligands of water molecules are common between $\text{Nd}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c})$ and octahydrate Nd^{3+} (aq) (Kawabe et al., 2006). In contrast, the case of (10) for the pair of Ln-DTPA(aq) and $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}(\text{c})$ having the same CN of 9, approximately represents a small nephelauxetic effect due to the different covalency of ligands between DTPA^{5-} and water molecules. The tetrad effect of ΔH_f for the formation of aqueous Ln-DTPA complex series with CN=9 provides a clue to distinguish the nephelauxetic effects by the different Ln(III)-ligand distances and by the different intrinsic covalency of ligands.

The plots of Figs. 3 and 4 are showing that thermochemical data for La-DTPA and Lu-DTPA are anomalous relative to those for the other members of Ln-DTPA series. If we accept the conclusion by the multinuclear NMR study (Peters, 1988), we have to

understand that the anomalous thermochemical data for La-DTPA and Lu-DTPA involve the unusually large experimental errors, and that all members of Ln(III)-DTPA are forming isostructural structures of the inner coordination spheres with CN=9 for Ln³⁺. This interpretation seems to be more acceptable than to assume different structures for La and Lu members from the isostructural ones for the other Ln members.

5) Toward systematic understanding of variable series trends of logK for Ln(III) complex formations

Staveley et al. (1966 and 1968) were the first to point out the importance of ΔH_r data for aqueous Ln(III) complex formations in couple with ΔH_r data for solution of the isomorphous series of Ln(ES)₃·9H₂O. They made the sums of their ΔH_r data for solution of Ln(ES)₃·9H₂O and the ΔH_r data for the (1:3) Ln-diglycolate and Ln-dipicolinate complex formations, and showed that the combined ΔH_r data exhibit regular monotonous trends composed of two small crescents making cusps at Gd. They suggested that the two aqueous Ln(III) complex series are isomorphous, and that the resultant regular curves with cusps at Gd are due to the ligand-field effects. Carson et al. (1968) followed Staveley et al. (1966), and they combined their ΔH_r data for Ln-DTPA formations with the ΔH_r data for solution of Ln(ES)₃·9H₂O reported by Staveley et al. (1966). The combined ΔH_r data showed an apparently irregular series change, unlike the results of Staveley et al. (1966). So that Carson et al. (1968) interpreted that the hydration state of Ln-DTPA is changing about halfway through the series. The irregular series change found by Carson et al. (1968), however, was biased by the insufficient ΔH_r

data for solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ by Staveley et al. (1966).

Kawabe (1999a) re-evaluated ΔH_r , ΔS_r , and ΔG_r data for solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ by using the experimental data by Staveley et al. (1968) and the others, those data for solution of $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ with $n=7$ and 6 (Spedding et al., 1977), and the improved RSPET equation (Kawabe, 1992). The data sets by Kawabe (1999a) provide the plots of Fig. 4. Furthermore, the regular curves with cusps at Gd interpreted as the ligand-field effects by Staveley et al. (1966 and 1968) are, in fact, the tetrad effects due to the nephelauxetic effects originating from the differences in Racah (E^1 and E^3) parameters. The improved RSPET equation (2) can well reproduce the fine features of the series variations of the thermodynamic data (Figs. 3 and 4). There are no terms for the ligand-field effects in the equation (2), because ligand-field effects like the cases of $(3d)^q$ metal ion complexes are less important than the nephelauxetic effects due to the interelectron repulsion of $4f$ electrons perturbed by bonding of Ln^{3+} with ligands (Jørgensen, 1979; Thompson, 1979).

Our conclusions concerning Racah parameters of Ln^{3+} in $\text{Ln}(\text{III})\text{-DTPA}$ and their structures in the present study are significantly different from those by Carson et al. (1968). The causes of the different conclusions by Carson et al. (1968) from ours are apparent: Our understanding of hydration changes in $\text{Ln}^{3+}_{(\text{aq})}$ series has much advanced in recent twenty years (Rizkalla and Choppin, 1991), and the thermodynamic data for solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ series (Kawabe, 1999a) used in this study are much more reliable than those used by Carson et al. (1968). The improve RSPET equation (Kawabe, 1992) plays a crucial role in examining the thermodynamic data in this study, whereas Carson et al. (1968) did not pay any attention to Jørgensen's RSPET. Two years after the publication of

Carson et al. (1968), Jørgensen (1970) and Nugent (1970) clarified the important relevance of RSPET to the thermodynamics of Ln(III) complex formations in relation to the empirical proposal of tetrad effect by Peppard et al. (1969).

Unfortunately, even today, many REE chemists and geochemists seem to reluctant to pay attention to Jørgensen's RSPET and the nephelauxetic effects in Ln(III) complexes which are totally different from the ligand-field effects in $(3d)^q$ metal ion complexes. The present results for Ln-DTPA formations illustrate the importance of Jørgensen's RSPET and the thermodynamic data combined with those for solution of $\text{Ln}(\text{ES})_3 \cdot 9\text{H}_2\text{O}$ series (Staveley et al., 1966 and 1968; Kawabe, 1999a). They may contribute to remove skeptical views about the tetrad effect in the lanthanide solution chemistry and geochemistry.

Kawabe (1999a, b) pointed out that the series variation of $\log K = -\Delta G_r / (2.303RT)$ for aqueous Ln(III) complex formations, in general, consists of the following four variation components:

- (1) the effect of hydration change of light $\text{Ln}^{3+}_{(\text{aq})}$ relative to heavy $\text{Ln}^{3+}_{(\text{aq})}$,
- (2) a tetrad effect variation including Gd-break when Racah (E^1 and E^3) parameters for Ln^{3+} are different between Ln(III) complex and $\text{Ln}^{3+}_{(\text{aq})}$,
- (3) irregular variations when the structural or hydration changes are occurring across the Ln(III) complex series of interest, and
- (4) the residual series variation given by a smooth function of the number of 4f electrons ($q = Z - 57$).

The thermodynamic data for Ln(III)-DTPA complex formations examined here provide

additional important points: Referring to eq. (7), the previous point (2) corresponds to the cases of $\Delta H_r(tetrad) \neq 0$ and $(1 - \kappa \cdot T) > 0$. The present study of thermodynamic data for Ln(III)-DTPA complex formation has revealed that such a case that $\Delta H_r(tetrad) \neq 0$ but $(1 - \kappa \cdot T) \approx 0$ is really important. The previous point (2) is modified into the following statement that "a tetrad effect variation including Gd-break is involved in logK, when Racah (E^1 and E^3) parameters for Ln^{3+} are different between Ln(III) complex and $Ln^{3+}_{(aq)}$, together with the condition that $\Delta H_r(tetrad) \neq T\Delta S_r(tetrad)$." The subtle tetrad effect or its absence in the series variation of logK for aqueous Ln(III) complex formation corresponds to either the situation of $\Delta H_r(tetrad) \approx 0$ or that of $\Delta H_r(tetrad) \approx T\Delta S_r(tetrad) \neq 0$. Smooth series variations of logK are not the immediate evidence against the tetrad effect as long as obvious tetrad effects are recognized in ΔH_r and ΔS_r .

Although the discussion by Kawabe (1999a, b) dealt with only the series variation of $\log K = -\Delta G_r / (2.303RT)$, the present study showed that all the thermodynamic data of ΔH_r , ΔS_r , and ΔG_r , when necessary corrections are made for them, can be fitted to the improved RSJET equation (2). Eventually, we have realized that the relationship that $\Delta G_r(tetrad) = \Delta H_r(tetrad) - T\Delta S_r(tetrad) \approx (1 - \kappa \cdot T)\Delta H_r(tetrad)$ holds true. The new viewpoints raised in this study will help gain a more comprehensive understanding of a variety of characteristic variations of not only ΔG_r (logK) but also ΔH_r and ΔS_r for aqueous Ln(III) complex formations including those of geochemical interest.

Conclusions

The series variations of experimental ΔH_r , ΔS_r and ΔG_r for the aqueous Ln-DTPA

complex formations at 27°C and an ionic strength of 0.1 M (Carson et al, 1968) have been re-examined from the viewpoints of the improved RSPET equation (Kawabe, 1992), the hydration changes of light $\text{Ln}^{3+}_{(\text{aq})}$ series (Kawabe, 1999a), and the inner coordination state of Ln^{3+} in Ln-DTPA complex series. The conclusions are as follows:

- 1) The ΔH_r , ΔS_r and ΔG_r data become compatible with the improved RSPET equation, when they are corrected for hydration changes in light $\text{Ln}^{3+}_{(\text{aq})}$ relative to heavy $\text{Ln}^{3+}_{(\text{aq})}$ series (Kawabe, 1999a), anomalous data for La-DTPA and Lu-DTPA relative to the others, and small experimental errors for Dy-DTPA and Er-DTPA. Racah (E^1 and E^3) parameters of Ln-DTPA are systematically greater than those of octahydrate $\text{Ln}^{3+}_{(\text{aq})}$: $\Delta E^1 = +(17 \pm 7) \text{ cm}^{-1}$ and $\Delta E^3 = +(10 \pm 2) \text{ cm}^{-1}$ for Ln=Nd.
- 2) The corrected data of ΔH_r and ΔS_r exhibit similar convex tetrad effects, whereas the data of ΔG_r show a fairly smooth variation with a subtle tetrad effect. The data of ΔH_r and ΔS_r fitted to the improved RSPET equation show that $\Delta S_r(\text{tetrad}) \approx \kappa \cdot \Delta H_r(\text{tetrad})$ with $\kappa(E^1) = (2.9 \pm 1.5) \times 10^{-3} (1/K)$ for the octad effect and $\kappa(E^3) = (2.4 \pm 0.7) \times 10^{-3} (1/K)$ for the intrinsic tetrad effect. The tetrad effect of ΔG_r is given by the tetrad effects of ΔH_r and ΔS_r : $\Delta G_r(\text{tetrad}) = \Delta H_r(\text{tetrad}) - T\Delta S_r(\text{tetrad}) \approx (1 - \kappa \cdot T)\Delta H_r(\text{tetrad})$. In the case of Ln-DTPA formation at $T \approx 300 \text{ K}$, it follows that $[1 - \kappa(E^1) \cdot T] \approx 0.1$ and $[1 - \kappa(E^3) \cdot T] \approx 0.3$. Thus $\Delta H_r(\text{tetrad})$ is cancelled by $T\Delta S_r(\text{tetrad})$ in $\Delta G_r(\text{tetrad})$ almost totally.
- 3) The thermochemical data for Ln-DTPA formations are illustrating that $\Delta H_r(\text{tetrad})$ competing with $T\Delta S_r(\text{tetrad})$ in $\Delta G_r(\text{tetrad})$ can produce an apparently smooth variation of $\log K = -\Delta G_r / (2.303RT)$. This point has been overlooked in the previous studies, but it

is important when considering a variety of logK for Ln(III) complex formations including those of geochemical interest.

4) Ln-DTPA complex formations, when combined with the solution reactions of the fully isomorphous Ln(III) ethylsulphate nonahydrate series (Ln(ES)₃·9H₂O), give the reactions that $Ln(ES)_3 \cdot 9H_2O_{(c)} + DTPA^{5-}_{(aq)} = [Ln - DTPA]^{2-}_{(aq)} + 3ES^{-}_{(aq)} + 9H_2O_{(l)}$, in which Ln³⁺_(aq) are eliminated. The series variations of thermodynamic parameters for the reactions regressed by RSPET, exhibit smooth patterns with a subtle tetrad effect.

5) Ln-DTPA series have Racah (E¹ and E³) parameters comparable with those of Ln(ES)₃·9H₂O: E¹ and E³ values relative to Ln(ES)₃·9H₂O for Ln=Nd are ΔE¹(Nd)=- (6±6) cm⁻¹ and ΔE³(Nd)=+(4±2) cm⁻¹. In spite of the octadentate ligand of DTPA, the coordination number (CN) of Ln³⁺ in Ln(III)-DTPA is possibly nine like Ln(ES)₃·9H₂O series. This is consistent with the reported results of CN=9 by the fluorescence kinetic measurements of Ln-DTPA (Ln=Eu,Tb, Dy and Yb), the XAFS study of Gd-DTPA, multinuclear NMR study of Ln-DTPA series, and X-ray structural studies of hydrate salts of Ln-DTPA complexes. As far as the multinuclear NMR study of Ln-DTPA series is accepted, the anomalous thermochemical data for La-DTPA and Lu-DTPA are biased by some unexpectedly large experimental errors.

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Figure Captions

Fig. 1. Series variations of logK for selected (1:1) Ln(III)- and Y(III)-chelate complex series. DTPA=diethylenetriaminepentaacetate, EDTA=ethylenediaminetetraacetate, NTA=nitrilotriacetate, dipic=dipicolinate. Data are cited from Moeller (1973) except for those of Ln-EDTA (Suzuki, 1999). The experimental conditions are 25°C and ionic strength of 0.1 M except for the temperature for Ln-NTA (20°C). The constants (C) for vertical displacements in the plot are given by the parenthesized figures.

Fig. 2. The series variations of experimental data (filled circles) for ΔH_r , ΔS_r , and ΔG_r for Ln(III)-DTPA complex formations (Carson et al., 1968) summarized in Table 1, and their corrected values (open circles) for the hydration changes of light $\text{Ln}^{3+}_{(\text{aq})}$ relative to the heavy $\text{Ln}^{3+}_{(\text{aq})}$ of octahydrate series (Kawabe, 1999a).

Fig. 3. The thermodynamic data for Ln(III)-DTPA formations with corrections for the hydration changes of light $\text{Ln}^{3+}_{(\text{aq})}$ relative to heavy $\text{Ln}^{3+}_{(\text{aq})}$ (Kawabe, 1999a), can be regressed to the improved RSPET equation (2) by the method of least squares. "hyc" denotes that they are corrected for the hydration changes of light $\text{Ln}^{3+}_{(\text{aq})}$. Filled symbols show such "hyc" data, but the data points for La, Dy, Er, and Lu (open symbols) are used in the regression in place of the data of filled symbols (see Table 1). The two continuous curves with smaller circles and crosses show the results of regressions and the smooth variation components, respectively. The differences between the two curves is the tetrad effect variation given by the second and third terms of eq. (2). The root-mean-square

errors in the regressions are 0.5 kJ/mol for $\Delta H_r(\text{hyc})$, 1.2 J/mol/K for $\Delta S_r(\text{hyc})$, and 0.4 kJ/mol for $\Delta G_r(\text{hyc})$.

Fig. 4. The series variations of the sums of thermodynamic data of Ln(III)-DTPA complex formations and those for the solution of the fully isomorphous Ln(ES)₃·9H₂O series (Kawabe, 1999a). They can be regressed by the improved RSPET equation (2), in which the data of Ln-DTPA formations with Ln=La, Dy, Er, and Lu corrected in the same way as in Fig. 3 (open symbols) and the uncorrected values (filled symbols) for the other Ln's. Each sum of two ΔG values is plotted as the sum plus 70 kJ/mol. The continuous curves with smaller circles and small crosses are the regression results and the smooth components of eq. (2), respectively. The differences between the two continuous curves is the tetrad effect variation given by the second and third terms of eq. (2). The root-mean-square errors in the regressions are 0.5 kJ/mol for ΔH , 1.1 J/mol/K for ΔS , and 0.4 kJ/mol for ΔG .

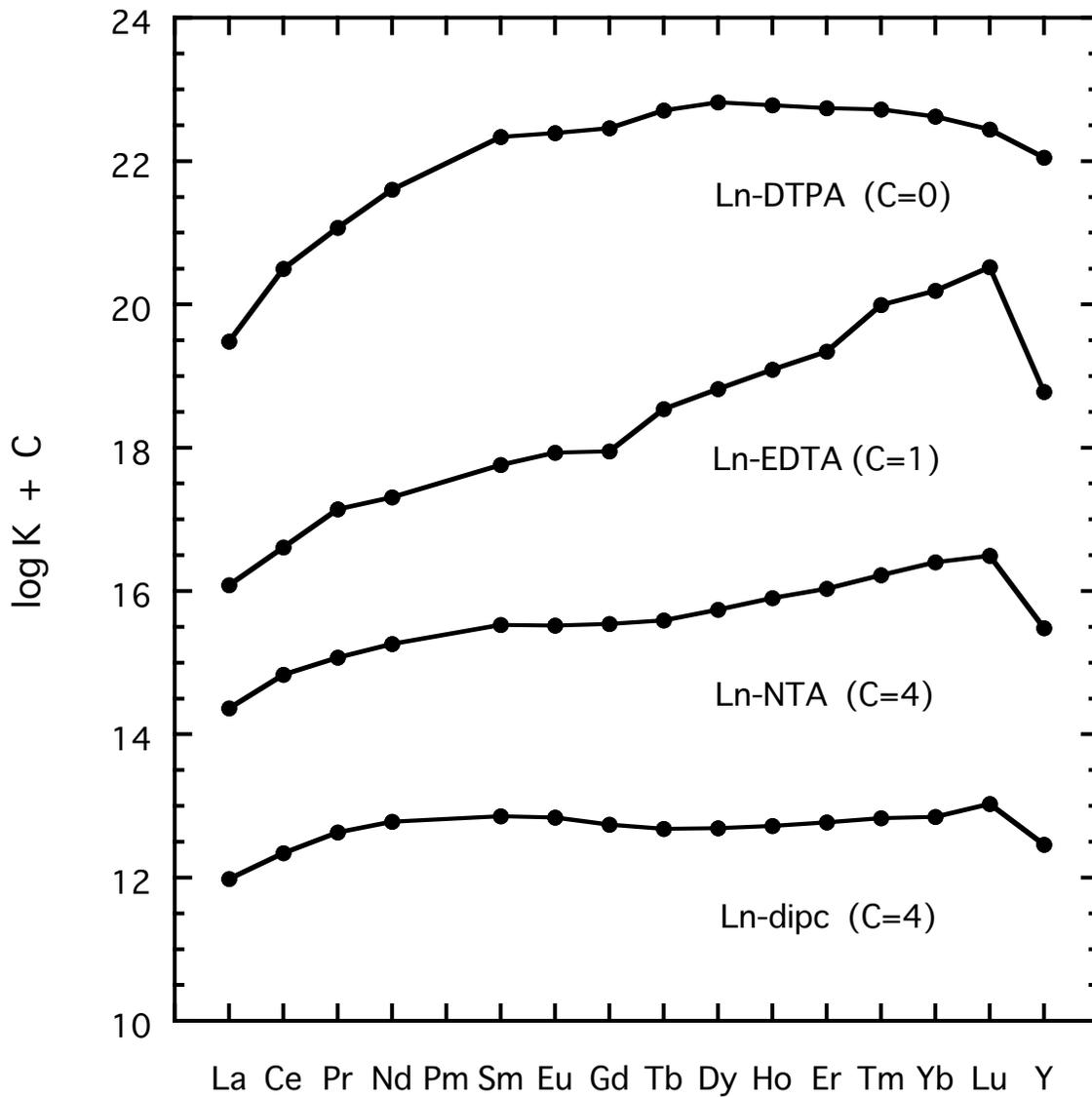


Fig. 1. (I. Kawabe)

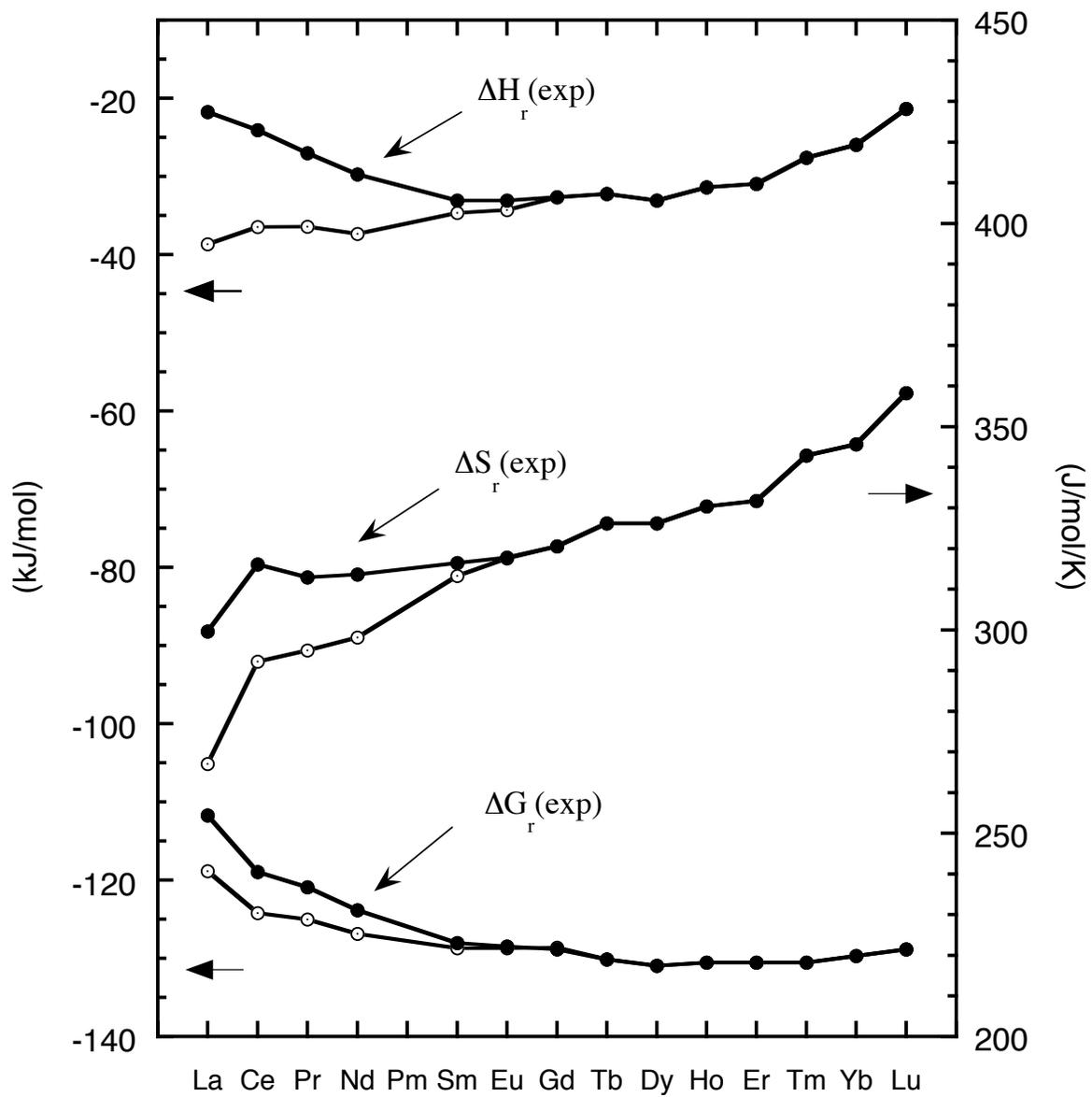


Fig. 2. (I. Kawabe)

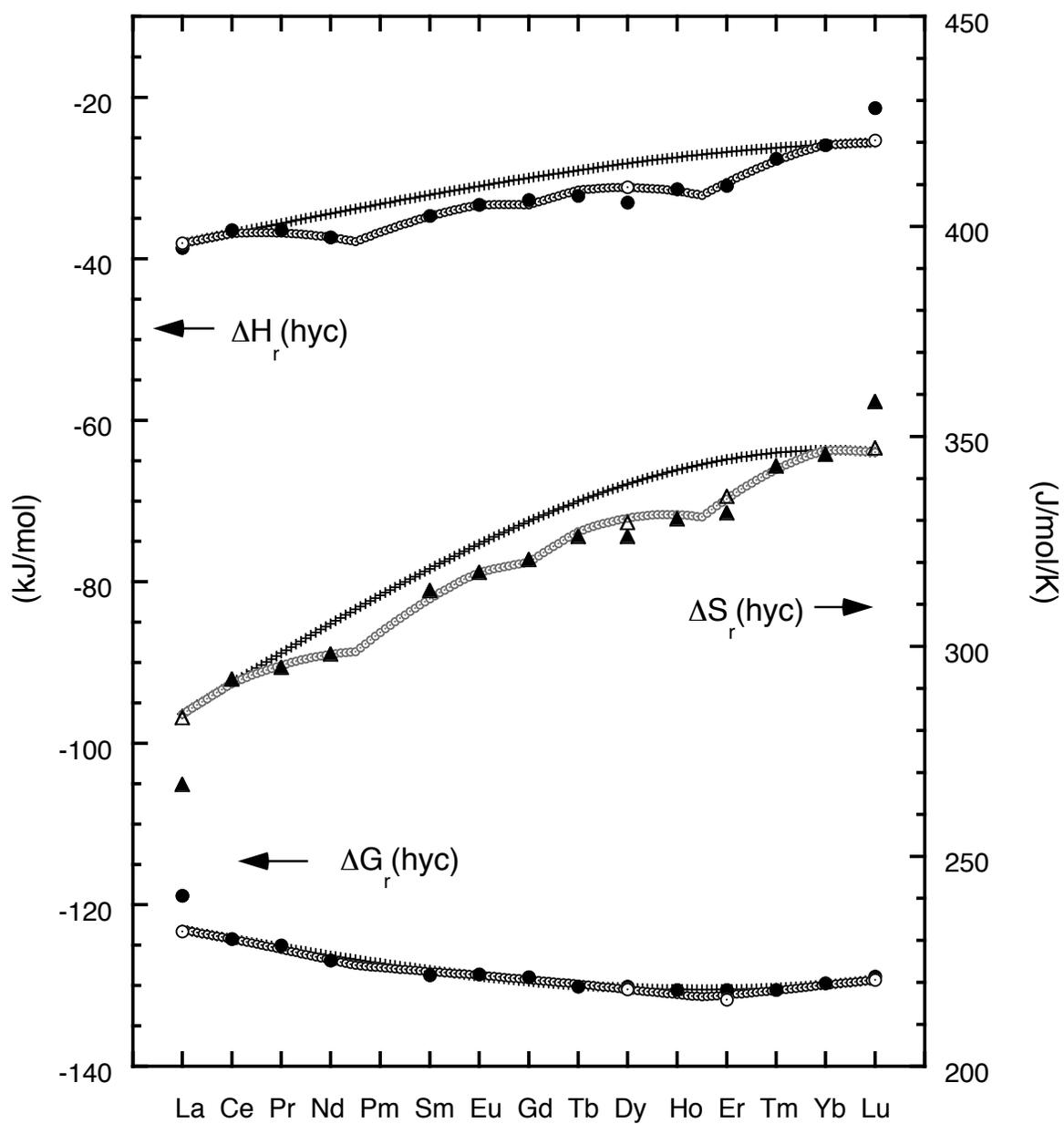


Fig. 3. (I. Kawabe)

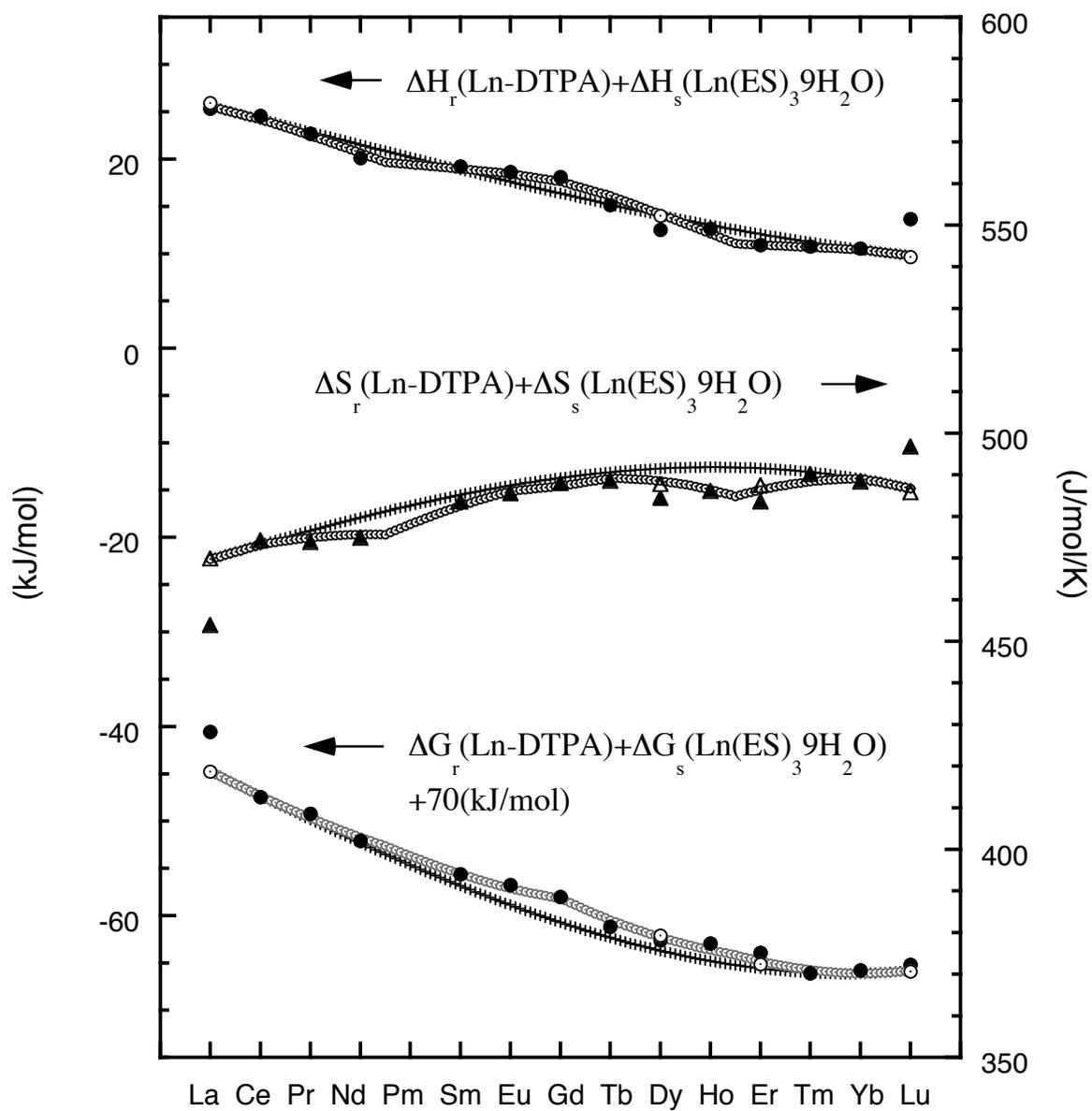


Fig. 4. (I. Kawabe)

Table 1. Thermodynamic data for Ln(III)-DTPA complex formations at 27°C after Carson et al. (1968)*

	ΔG_r (kJ/mol)	ΔH_r (kJ/mol)	ΔS_r (J/mol/K)
La	-111.7, (-115.9)**	-21.8, (-21.2)**	299.7, (315.7)**
Ce	-118.9	-24.1	316.1
Pr	-120.9	-27.0	313.0
Nd	-123.9	-29.7	313.6
Sm	-128.0	-33.1	316.4
Eu	-128.5	-33.1	317.8
Gd	-128.9	-32.6	320.6
Tb	-130.1	-32.2	326.2
Dy	-131.0, (-130.5)†	-33.1, (-31.6)†	326.2, (329.5)†
Ho	-130.5	-31.4	330.4
Er	-130.5, (-131.7)†	-31.0	331.8, (335.8)†
Tm	-130.5	-27.6	342.9
Yb	-129.7	-25.9	345.7
Lu	-128.9, (-129.6)**	-21.3, (-25.3)**	358.3, (347.3)**

* Carson et al. (1968) did not list the ΔG_r and ΔS_r values for Ce-DTPA. The ΔG_r value is calculated in this study from $\log K=20.5$ at 25°C for Ce-DTPA (Moeller et al., 1965), corrected to 27°C. ΔS_r [$=(\Delta H_r-\Delta G_r)/T$] is calculated from the ΔG_r value and the ΔH_r value by Carson et al. (1968).

** The parenthesized figures for La-DTPA and Lu-DTPA are those values estimated by the regression to the RSPET equation (2) shown in Figs. 3 and 4.

† The parenthesized figures for Dy-DTPA and Er-DTPA are the values by the least-squares fittings to the RSPET equation (2) shown in Figs. 3 and 4.

Table 2-A. C_1 and C_3 parameter values in the RSPET equation (2) fitted to the thermodynamic data for Ln(III)-DTPA complex formations (Fig. 3)

	$C_1/10^{-2}$	$C_3/10^{-3}$
ΔH_r (kJ/mol)	(0.71±0.28)	(4.3±0.9)
ΔS_r (J/mol/K)	(2.1±0.7)	(10.3±2.2)
ΔG_r (kJ/mol)	-(0.05±0.2)	(0.9±0.7)
$\Delta G_r = \Delta H_r - T\Delta S_r$ (kJ/mol)*	(0.08±0.3)	(1.2±1.1)

* Calculations by $C_i(\Delta G_r) = C_i(\Delta H_r) - T C_i(\Delta S_r)$ and $T=300$ K for $i=1$ and 3 from the C_1 and C_3 values in the first and second rows.

Table 2-B. C_1 and C_3 parameter values in the RSPET equation (2) fitted to the thermodynamic data for Ln(III)-DTPA formations combined with those for solution of Ln(III) ethylsulphate nonahydrates (Fig. 4)

	$C_1/10^{-2}$	$C_3/10^{-3}$
ΔH_r (kJ/mol)	-(0.27±0.27)	(1.8±0.9)
ΔS_r (J/mol/k)	(0.43±0.63)	(6.5±2.0)
ΔG_r (kJ/mol)	-(0.55±0.25)	-(0.50±0.81)
$\Delta G_r = \Delta H_r - T\Delta S_r$ (kJ/mol)*	-(0.40±0.33)	-(0.18±1.1)

* Calculations by $C_i(\Delta G_r) = C_i(\Delta H_r) - T C_i(\Delta S_r)$ and $T=300$ K for $i=1$ and 3 from the C_1 and C_3 values in the first and second rows.