

Table 1. Experimental thermodynamic data for Ln-EDTA complex formation.

	Mackey et al. (1962)			This study	
	$\Delta H_r$ (kJ/mol)	$\Delta G_r^a)$ (kJ/mol)	$\Delta S_r$ (J/mol/K)	$\Delta G_r^b)$ (kJ/mol)	$\Delta S_r^c)$ (J/mol/K)
La	-12.24	-86.69	249.8	-85.92 ± 0.69	247.1
Ce	-12.29	-88.16	254.4	-88.49± 0.40	255.6
Pr	-13.38	-89.91	256.9	-90.83± 0.46	259.8
Nd	-15.16	-91.59	256.5	-92.26± 0.46	258.6
Sm	-14.01	-94.31	269.4	-95.06± 0.46	271.8
Eu	-10.70	-95.06	282.8	-95.97± 0.51	286.0
Gd	-7.24	-95.98	297.9	-96.31± 0.29	298.7
Tb	-4.66	-98.83	315.9	-99.43± 0.34	317.9
Dy	-5.07	-101.46	323.4	-101.56± 0.40	323.6
Ho	-5.67	-102.97	326.4	-102.88± 0.57	326.0
Er	-7.15	-104.85	327.6	-104.59± 0.63	326.8
Tm	-7.82	-106.44	331.0	-107.16± 0.40	333.2
Yb	-9.67	-108.41	331.4	-108.42± 0.23	331.2
Lu	-10.51	-109.24	331.0	-109.90± 0.51	333.4
Y	-2.46	-99.16	324.3	-100.59	329.1
	25°C, $\mu=0.1(\text{KNO}_3)$	25°C, $\mu=0.1(\text{KCl})$		25°C, $\mu=0.1(\text{KCl or KNO}_3)$	

a) Values calculated from  $\Delta H$  here and  $\log K$  values reported by Betts and Dahlinger (1959) .

b) Re-evaluated averages and two sigma S.D. from the experimental data of  $\log K$  by five different methods (Kawabe, 2013a). Since  $\log K(\text{Y})=17.62$  at 25°C and  $\mu=0.1(\text{KCl or KNO}_3)$  was fixed for normalization of all the data, its S. D. value is not evaluated.

c) Calculated values from  $\Delta H_r$  by Mackey et al. (1962) and  $\Delta G_r$  by Kawabe (2013a).

Table 2. A:  $\Delta G_r(\text{hyc})$ ,  $\Delta H_r(\text{hyc})$ , and  $\Delta S_r(\text{hyc})$  for the formation of  $[\text{LnEDTA}(\text{H}_2\text{O})_3]\Gamma^{(\text{aq})}$  and  $[\text{LnEDTA}(\text{H}_2\text{O})_2]\Gamma^{(\text{aq})}$  from octahydrate of  $\text{Ln}^{3+}_{(\text{aq})}$ , and B:  $\Delta\Delta G_r^0$ ,  $\Delta\Delta H_r^0$ ,  $\Delta\Delta S_r^0$ , and  $\Delta\Delta S_r^0$  for the hydration change reaction between the two Ln-EDTA series.

	A <sup>1)</sup>						B <sup>2)</sup>		
	$\Delta G_r(\text{hyc})^{\text{e)}$		$\Delta H_r(\text{hyc})^{\text{e)}$		$\Delta S_r(\text{hyc})^{\text{d)}$		$\Delta\Delta G_r^0$	$\Delta\Delta H_r^0$	$\Delta\Delta S_r^0$
	CN=9	CN=8	CN=9	CN=8	CN=9	CN=8			
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	J/mol/K	J/mol/K	kJ/mol	kJ/mol	J/mol/K
La	<b>-93.08</b>	-71.00	<b>-29.14</b>	10.00	<b>214.5</b>	271.7	22.1	39.14	57.2
Ce	<b>-93.76</b>	-76.50	<b>-24.69</b>	7.70	<b>231.7</b>	282.4	17.3	32.4	50.8
Pr	<b>-94.92</b>	-81.00	<b>-22.83</b>	5.50	<b>241.8</b>	290.1	13.9	28.3	48.3
Nd	<b>-95.28</b>	-84.50	<b>-22.80</b>	4.00	<b>243.1</b>	296.8	10.8	26.8	53.7
Pm	(-95.20)	(-88.40)	(-21.50)	(2.00)	(247.2)	(303.2)	(6.8)	(23.5)	(56.0)
Sm	-94.80	-91.70	-20.50	1.00	249.2	310.9	3.1	21.5	61.7
Eu	-94.14	-94.14	-20.50	-0.80	247.0	313.1	0.0	19.7	66.1
Gd	-94.20	-95.50	-20.50	-0.20	247.2	319.6	-1.3	20.3	72.5
Tb	-93.05	-99.00	-18.50	-3.10	250.0	321.7	-6.0	15.4	71.6
Dy	-91.50	<b>-101.56</b>	-17.50	<b>-5.07</b>	248.2	<b>323.6</b>	-10.1	12.4	75.4
Ho	-91.00	<b>-102.88</b>	-16.50	<b>-5.67</b>	249.9	<b>326.0</b>	-11.9	10.8	76.2
Er	-89.05	<b>-104.59</b>	-16.00	<b>-7.15</b>	245.0	<b>326.8</b>	-15.5	8.9	81.8
Tm	-87.27	<b>-107.16</b>	-14.40	<b>-7.82</b>	244.4	<b>333.2</b>	-19.9	6.6	88.8
Yb	-85.70	<b>-108.42</b>	-13.00	<b>-9.67</b>	243.8	<b>331.2</b>	-22.7	3.3	87.4
Lu	-84.50	<b>-109.90</b>	-13.00	<b>-10.51</b>	239.8	<b>333.4</b>	-25.4	2.5	93.5

1) For the reaction (20-1) of  $[\text{LnEDTA}(\text{H}_2\text{O})_2]\Gamma^{(\text{aq})}$  with  $\text{CN}(\text{Ln}^{3+})=8$  and the reaction (20-2) of  $[\text{LnEDTA}(\text{H}_2\text{O})_3]\Gamma^{(\text{aq})}$  with  $\text{CN}(\text{Ln}^{3+})=9$ .

The values in *gothic* for the light Ln or the heavy Ln are the experimental ones, because each Ln-EDTA is regarded as the single species.

2) For the hydration change reaction (3) that  $[\text{LnEDTA}(\text{H}_2\text{O})_3]\Gamma^{(\text{aq})} = [\text{LnEDTA}(\text{H}_2\text{O})_2]\Gamma^{(\text{aq})} + \text{H}_2\text{O}_{(l)}$ . They are given by the differences between the respective pairs of CN=8 and CN=9 in Part A of this table.

Table 3. A: Experimental  $\Delta G_r(\text{hyc})$ ,  $\Delta H_r(\text{hyc})$ , and  $\Delta S_r(\text{hyc})$  for Ln-EDTA formation from *octahydrate of Ln<sup>3+</sup>(aq)* compared with the calculated ones by our model of eq. (16-1), (16-2), and (16-3). B:  $\Delta \Delta G_r^0$ ,  $\Delta \Delta H_r^0$ , and  $\Delta \Delta S_r^0$  for the hydration change reaction between the two Ln-EDTA series in Table 2 and their regression values by the RSPET equation of (21).

	A <sup>1)</sup>						B <sup>2)</sup>					
	$\Delta G_r(\text{hyc})$		$\Delta H_r(\text{hyc})$		$\Delta S_r(\text{hyc})$		$\Delta \Delta G_r^0$		$\Delta \Delta H_r^0$		$\Delta \Delta S_r^0$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Input	RSPET	Input	RSPET	Input	RSPET
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	J/mol/K	J/mol/K	kJ/mol	kJ/mol	kJ/mol	kJ/mol	J/mol/K	J/mol/K
La	-93.08	-93.08	-29.14	-29.13	214.5	214.5	22.1	21.6	39.14	37.6	57.2	53.3
Ce	-93.76	-93.76	-24.69	-24.66	231.7	231.8	17.3	17.2	32.4	32.7	50.8	51.4
Pr	-94.92	-95.31	-22.83	-22.73	241.8	242.2	13.9	13.9	28.3	29.7	48.3	52.4
Nd	-95.28	<b>-95.31</b>	-22.80	<b>-22.46</b>	243.1	<b>244.4</b>	<b>10.8</b>	11.3	<b>26.8</b>	27.9	<b>53.7</b>	55.6
Pm		<b>-95.35</b>		<b>-20.08</b>		<b>252.5</b>		8.0		25.4		58.4
Sm	-95.60	<b>-95.42</b>	-15.62	<b>-15.71</b>	268.3	<b>267.4</b>	<b>3.1</b>	3.8	<b>21.5</b>	22.0	<b>61.7</b>	60.8
Eu	-96.14	<b>-95.86</b>	-10.94	<b>-10.65</b>	285.8	<b>285.8</b>	<b>0.0</b>	0.4	<b>19.7</b>	20.0	<b>66.1</b>	65.6
Gd	-96.37	<b>-96.65</b>	-7.30	<b>-7.75</b>	298.7	<b>298.2</b>	<b>-1.3</b>	-1.5	<b>20.3</b>	20.6	<b>72.5</b>	74.3
Tb	-99.45	<b>-99.22</b>	-4.66	<b>-4.38</b>	317.9	<b>318.1</b>	<b>-6.0</b>	-6.5	<b>15.4</b>	14.9	<b>71.6</b>	71.7
Dy	-101.56	<b>-101.60</b>	-5.07	<b>-5.28</b>	323.6	<b>323.1</b>	<b>-10.1</b>	-10.0	<b>12.4</b>	11.8	<b>75.4</b>	72.7
Ho	-102.88	-102.90	-5.67	-5.76	326.0	325.8	-11.9	-12.5	10.8	10.3	76.2	76.4
Er	-104.59	-104.59	-7.15	-7.17	326.8	326.8	-15.5	-15.9	8.9	8.0	81.8	79.5
Tm	-107.16	-107.16	-7.82	-7.82	333.2	333.2	-19.9	-20.0	6.6	4.7	88.8	81.9
Yb	-108.42	-108.42	-9.67	-9.67	331.2	331.2	-22.7	-23.2	3.3	3.2	87.4	87.3
Lu	-109.90	-109.90	-10.51	-10.51	333.4	333.4	-25.4	-24.3	2.5	5.0	93.5	97.3

1) "Exp." values are after  $\Delta G_r$  (Kawabe, 2013a) and  $\Delta H_r$  (Mackey et al., 1962) in Table 1 with the corrections for the hydration changes of light Ln<sup>3+</sup>(aq) series (Kawabe, 1999a). "Calc." values are calculated by eqs. 16-1), (16-2), and (16-3) for middle Ln.

2) The "Input" values are those in Part B of Table 2, and "RSPET" ones are the results when "input" values are regressed by eq. (21).

