The Thermodynamics of the Complexation of Lanthanides by 1-Hydroxy-4,7-disulfo-2-naphthoic Acid

LAURI H. J. LAJUNEN*, MARJA LAJUNEN* and GREGORY R. CHOPPIN

Department of Chemistry, Florida State University, Tallahassee, Fla. 32306-3006, U.S.A.

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Abstract

The thermodynamic parameters, log β, ΔH and ΔS, for formation of lanthanide–1-hydroxy-4,7-disulfo-2-naphthoic acid complexes have been determined at 25 °C in 0.10 M $NaClO_4$ solutions by potentiometric and calorimetric titrations. Under the experimental conditions, the data can be explained with the formation of LnL^-, LnL_2^{5-} and LnHL complexes (H_2L^{2-} = 1-hydroxy-4,7-disulfo-2-naphthoic acid anion). At pH < 3 the LnHL complex is the major species, whereas by increasing pH the formation of LnL_n^{3-4n} complexes becomes more important. The data are compared to the comparable data for complexing by aromatic carboxylic acids.

Introduction

Recently, the thermodynamic parameters for formation of the lanthanide complexes with 5-sulfosalicylic acid were studied [1]. The stability constants for lanthanide complexes with 3,5-disulfosalicylic acid [2], 3-hydroxy-7-sulfo-2-naphthoic acid [3] and 1-hydroxy-4-sulfo-2-naphthoic acid [4] also have been reported earlier. In this paper, we describe the results of potentiometric and calorimetric titrations of lanthanides with 1-hydroxy-4,7-disulfo-2-naphthoic acid (Fig. 1) in 0.10 M ($NaClO_4$) solution at 25 °C.

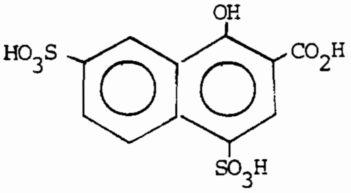

Fig. 1. 1-Hydroxy-4,7-disulfo-2-naphthoic.

Experimental

Reagents

Sodium 1-hydroxy-4,7-disulfonato-2-naphthoic acid was prepared as reported earlier [5]. The purity of the compound was checked by titration with standardized NaOH and by ^1H NMR measurements [6].

The stock solutions of 1-hydroxy-4,7-disulfo-2-naphthoic acid were prepared by dissolving the reagent in deionized water after which the concentration was determined by titration with standardized NaOH solution. The ligand buffer solutions were prepared by mixing solutions of the acid and 1 M NaOH, then diluting the mixture to the desired concentrations (between 0.03 and 0.05 M).

The preparation and analysis of the lanthanide perchlorate stock solutions have been described earlier [7].

All other chemicals were reagent grade. All solutions were adjusted to 0.10 M ionic strength with $NaClO_4$.

Procedures and Calculations

Potentiometric measurements were made with a Corning pH meter 130 using a combination electrode. The electrode system was calibrated using standard buffer solutions of pH = 7.00 ± 0.01 and 4.00 ± 0.01. At the low pH region (pH < 4), corrected pH values were obtained from the measured pH values and a calibration plot of pH (meas.) *vs.* pH (corr.). This calibration plot was developed from titration of 0.10 M $NaClO_4$ solution with a standard $HClO_4$ solution. At pH > 4.5, a value of 0.782 was used for the hydrogen ion activity coefficient.

Two types of potentiometric titrations were performed to obtain the stability constants. In one method, the lanthanide perchlorate solution was titrated directly with a buffered ligand solution while in the second, a mixture of lanthanide perchlorate and ligand acid was titrated with 0.1 M NaOH solution. As the ligand can form two types of complexes ($Ln(HL)_n^{3-3n}$ and LnL_n^{3-4n}), titrations with the buffered ligand were performed at two pH levels.

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*On leave from the Department of Chemistry, University of Oulu, SF-90570 Oulu, Finland.

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In the first series the pH was maintained between 2.5 and 3, in which region the formation of Ln-$(HL)_n^{3-3n}$ could be expected to be dominant. The second series was performed at pH range 4 to 7 in which range LnL_n^{3-4n} complexes would be expected to form also. The total metal concentration, C_M, was varied between 0.001 and 0.015 M.

The calorimetric titrations were performed using a peltier-cooled calorimeter. The calorimeter and the titration procedure used have been described in detail earlier [8, 9]. Lanthanide perchlorate solutions were titrated with the partly neutralized ligand solution ($C_L \sim 0.045$ M and $[H_2L^{2-}] \sim 0.003$ M). The heats of dilution of the ligand buffer solution and lanthanide perchlorate solutions were also determined, as well as the heat of protonation of the ligand anion. All measurements were performed at 25.0 °C.

For the protonation constants of 1-hydroxy-4,7-disulfo-2-naphthoic acid, the values $\log K_1 = 11.12$ (pK_{a2}) and $\log K_2 = 2.21$ (pK_{a1}) were used for the calculations of the thermodynamic parameters [10]. These correspond to deprotonation of the phenolic and carboxylic groups, respectively. The calculations of the stability constants and the enthalpy values for the complexation of lanthanides by 1-hydroxy-4,7-disulfo-2-naphthoic acid from the potentiometric and calorimetric data have been described previously [7, 10].

TABLE I. Potentiometric Data for Complexation of La(III) by 1-Hydroxy-4,7-disulfo-2-naphthoic Acid. $I = 0.10$ ($NaClO_4$); $T = 25$ °C[a]

Titrant volume (ml)	pH	[L] (M)	$\bar{n}$ (experimental)
2.60	5.683	1.243e – 08	0.137
2.65	5.837	1.732e – 08	0.182
2.70	5.967	2.283e – 08	0.226
2.75	6.085	2.925e – 08	0.271
2.80	6.191	3.643e – 08	0.316
2.85	6.293	4.494e – 08	0.361
2.90	6.389	5.463e – 08	0.406
2.95	6.485	6.638e – 08	0.458
3.00	6.577	7.985e – 08	0.496
3.05	6.672	9.666e – 08	0.541
3.10	6.768	1.172e – 07	0.586
3.15	6.861	1.410e – 07	0.631
3.20	6.962	1.726e – 07	0.676
3.25	7.068	2.136e – 07	0.721
3.30	7.179	2.657e – 07	0.766
3.35	7.300	3.416e – 07	0.811
3.40	7.431	4.465e – 07	0.856
3.45	7.572	5.965e – 07	0.901
3.50	7.736	8.391e – 07	0.946
3.55	7.918	1.229e – 06	0.990
3.60	8.128	1.917e – 06	1.035

[a] Initial conditions: In cup; $C_M = 0.00222$ M; $C_H = 0.00978$ M; $C_L = 0.00488$ M; volume = 50 ml titrant; 0.10 M NaOH.

Results

Typical potentiometric titration data are presented in Table I and Table II for the pH range 5.6–8.1. Figure 2 is a plot of similar data for the pH range 2.4–3.2 expressed as $\bar{n}$ *vs.* –log (ligand concentration) where $\bar{n}$ = average number of ligand anions bound per metal cation. For the lower pH range, the dominant ligand species is HL^{3-} in which the two sulfonate and the carboxylate groups are ionized. In the higher pH region, the complexing species L^{4-} is present also. As a result, the stability constants, $\beta_{1(11)i}$, for the reaction:

$$Ln^{3+} + iHL^{3-} = Ln(HL)_i^{3-3i} \qquad (1)$$

can be calculated from the data of the $2.4 < pH < 3.2$ range. Although it was obvious from the data that $Ln(HL)^{3-}$ formed, no stability constants for that

TABLE II. Stability Constants for Lanthanide–1-Hydroxy-4,7-disulfo-2-naphthoic Acid Complexes. $I = 0.10$ ($NaClO_4$); $T = 25$ °C

Ln	$\log \beta_{1(11)}$ [b]	$\log \beta_{101}$ [b]	$\log \beta_{102}$ [c]	$\log k_{102}$	$\log(\beta_{101}/k_{102})$
La	2.01	7.08	11.7	4.6	2.5
Pr	2.06	7.61	12.7	5.1	2.5
Nd	2.07	7.85	12.5	4.6	3.2
Sm	2.25	8.49	14.2	5.7	2.8
Eu	2.22	8.71	14.6	5.9	2.8
Gd	2.06	8.67	14.5	5.8	2.8
Tb	1.94	8.85	14.7	5.9	3.0
Dy	1.89	8.95	14.7	5.8	3.2
Ho	1.92	8.86	14.7	5.8	3.0
Er	1.88	8.86	14.7	5.8	3.0
Tm	1.95	9.01	14.9	5.8	3.2
Yb	1.90	8.91	14.6	5.7	3.2
Lu	1.99	8.80	14.5	5.7	3.1

[a] ±0.06. [b] ±0.05. [c] ±0.2.

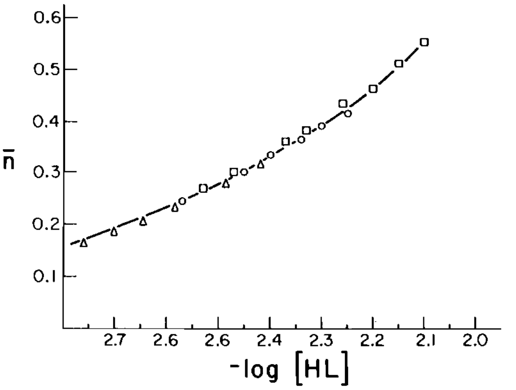

Fig. 2. Potentiometric data of Nd(III)–1-hydroxy-4,7-disulfo-2-naphthoic acid system obtained at $2.4 < pH < 3.2$ and plotted as curves $\bar{n}$ *vs.* $-\log[HL]$. The solid curve was calculated using $\log \beta_{1(11)} = 2.07$ and $\log \beta_{1(11)2} = 3.10$. Different symbols denote the following starting concentrations (mol/l). Cup solution: ○, $C_M = 0.00450$ and $C_H = 9.0e-05$; □, $C_M = 0.00821$ and $C_H = 3.2e-06$; △, $C_M = 0.00821$ and $C_H = 3.2e-06$. Titrant. ○, $C_L = 0.0500$ and $[H_2L] = 0.0150$; □, $C_L = 0.0510$ and $[H_2L] = 0.0160$; △, $C_L = 0.0510$ and $[H_2L] = 0.0200$.

species are reported as the maximum $\bar{n}$ values were too small to allow valid estimates. Figure 2 shows the agreement of data with the $\bar{n}$ values calculated from the log $\beta_{1(11)}$ values obtained by the computer analysis. Precipitation appeared in the titrations at higher pH where formation of the LnL_2 complexes occurs, restricting the highest $\bar{n}$ values to about 1.0–1.1. Consequently, the limits of error for the log β_{102} values are much higher than those for the log β_{101} values. Inclusion of log $\beta_{1(11)i}$ values in the computer analysis gave good values for log β_{101} for the reaction:

$$Ln^{3+} + iL^{4-} = LnL_i^{3-4i} \qquad (2)$$

Table II lists the calculated values of log $\beta_{1(11)}$, log β_{101} and log β_{102}. The standard deviations in the individual titrations for log $\beta_{1(11)}$, log β_{101}, log β_{102} and $\Delta H_{1(11)}$ were 0.002–0.008, 0.001–0.005, 0.015–0.030 and 0.02–0.08, respectively. The errors given in Table II are based on the agreement in repetitive titrations.

A typical set of calorimetric data is presented in Table III. In these titrations, only the protonated complexes of eqn. (1) form. However, the uncertainties in the log $\beta_{1(11)_2}$ and corresponding $\Delta H_{1(11)_2}$ are so large that we have not reported them. Table IV contains the thermodynamic parameters for the formation of Ln(HL)°.

TABLE III. Calorimetric Data for Complexation of Ho(III) by 1-Hydroxy-4,7-disulfo-2-naphthoic Acid. $I = 0.10$ ($NaClO_4$); $T = 25$ °C[a]

Titrant volume (ml)	Q (mJ)
0.5	−126
1.0	−220
1.5	−312
2.0	−403
2.5	−487
3.0	−563
3.5	−637
4.0	−702
4.5	−773
5.0	−840
5.5	−903
6.0	−963
6.5	−1025
7.0	−1068
7.5	−1126
8.0	−1180
8.5	−1238
9.0	−1298
9.5	−1337
10.0	−1377

[a] Initial conditions: In cup: $C_M = 0.00920$ M, pH = 3.818, volume = 50 ml, titrant; $C_M = 0.04272$ M, $C_H = 0.04544$ M.

TABLE IV. Thermodynamic Parameters for Formation of Ln(HL) Complexes. $I = 0.10$ ($NaClO_4$); $T = 25$ °C

Ln	$-\Delta G_{1(11)}$[a] (kJ/mol)	$\Delta H_{1(11)}$[b] (kJ/mol)	$\Delta S_{1(11)}$[c] (J/K)
La	11.44	4.2	52
Pr	11.73	2.1	46
Nd	11.79	2.6	48
Sm	12.82	2.9	53
Eu	12.65	4.0	56
Gd	11.73	7.0	63
Tb	11.05	6.2	58
Dy	10.77	6.7	59
Ho	10.94	8.4	65
Er	10.71	9.2	67
Tm	11.11	8.1	64
Yb	10.81	7.7	62
Lu	11.34	7.5	63
H	12.59	−1.7	37

[a] ±0.35 (based on repetitive titrations). [b] ±10% (based on repetitive titrations). [c] ±5%.

Discussion

Evidence for chelate formation in the aromatic *o*-hydroxycarboxylate complexation of lanthanides is seen in Fig. 3. In this figure, the stability constants of the Eu–*o*-hydroxycarboxylate complexes (log $\beta_{1(11)}$) show a linear correlation with pK_a (of the carboxylate group) which is more than an order of magnitude greater than the stability constant correlation line for the lanthanide benzoates (log β_{101}).

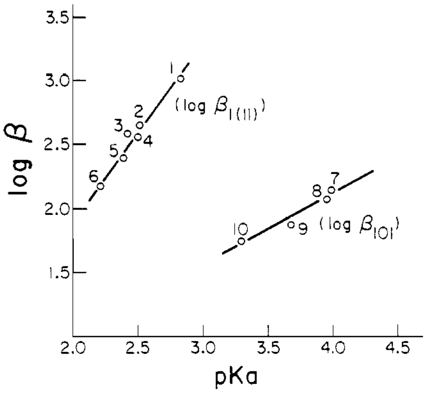

Fig. 3. Relationship between the stability constant of Eu(III) log $\beta_{1(11)}$ for o-hydroxy carboxylates or log β_{101} for benzoates, and the acid constant, pK_a, of the carboxylic group of the ligand. 1: 1-hydroxy-7-sulfo-2-naphthoic acid; 2: 3-hydroxy-7-sulfo-2-naphthoic acid; 3: 5-sulfosalicylic acid; 4: 1-hydroxy-4-sulfo-2-naphthoic acid; 5: 3-hydroxy-5-sulfo-2-naphthoic acid; 6: 1-hydroxy-4,7-disulfo-2-naphthoic acid; 7: benzoic acid; 8: 4-fluorobenzoic acid; 9: 3-fluorobenzoic acid; 10: 3-nitrobenzoic acid.

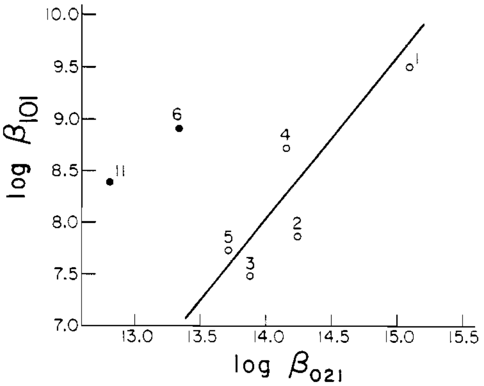

Fig. 4. Relationship betwen the stability constant, log β_{101}, for formation of EuL^- and ΣpK_a of H_2L^{2-}. 1: 1-hydroxy-7-sulfo-2-naphthoic acid; 2: 3-hydroxy-7-sulfo-2-naphthoic acid; 3: 5-sulfosalicylic acid; 4: 1-hydroxy-4-sulfo-2-naphthoic acid; 5: 3-hydroxy-5-sulfo-2-naphthoic acid; 6: 1-hydroxy-4,7-disulfo-2-naphthoic acid; 7: 3,5-disulfosalicylic acid.

As to be expected, the stability constants of β_{101} of the LnL^{1-} complexes in which the phenolic group of the aromatic o-hydroxycarboxylates is also deprotonated are much larger than the corresponding $\beta_{1(11)}$ values. Even though the strongly acidic sulfonic acid groups are not coordinated directly with the metal cation, they do influence the stability of the complexes. As we see in Fig. 4, the monosulfonate ligands roughly correlate with $pK_{a1} + pK_{a2}$ (phenolic + carboxylic deprotonation) but the disulfonate ligands are more stable. The explanation of this enhanced stability of complexation by the disulfonate ligands is not obvious. The scatter in the correlation for the monosulfonate ligands in Fig. 4 probably reflects error in the pK_{a1} values (phenolic dissociation) but the deviation of the two disulfonate ligands is too large to be explained as pK_a error. Also, comparison of Figs. 3 and 4 shows that the enhancement of stability related to the presence of two rather than a single sulfonate is present only in the LnL^{1-} species and not in $LnHL^0$. It has been proposed that the lanthanides can, via resonance and/or inductive effects, polarize electronic charge in aromatic ligands [11]. Canonical structures can be drawn for all the complexes of Fig. 4 which would provide such charge polarization on the phenoxy donor atom increasing the metal–ligand interaction. If this effect is operating in these systems, the disulfonate ligands allow more canonical structures, increasing the polarization enhancement.

The variation of log β_{101} with lanthanide atomic number shows a tetrad effect [12, 13] whereas log $\beta_{1(11)}$ shows no such correlation. Moreover, log β_{101} has an irregular increase with lanthanide atomic number while log $\beta_{1(11)}$ has a maximum at Sm(III) and is smaller for the *trans*-Gd cations than for La(III). The pattern (and tetrad effect) of log β_{101} is quite similar to that of the other aromatic o-hydroxycarboxylate complexes [1–4]. The general trend in log β_{101} resembles that of the lanthanide–dicarboxylate complexation [14] and of the log $\beta_{1(11)}$ of the aliphatic α-hydroxycarboxylate complexes [15]. However, the trend in log $\beta_{1(11)}$ in Table II resembles that for log β_{101} of the lanthanide maleates [16, 17]. Apparently, larger chelate rings favor the pattern observed for log $\beta_{1(11)}$ but this can be overcome if the bonding is stronger (as in log β_{101}).

Figure 5 shows the variation of the thermodynamic parameters of formation of LnHL where L = 5-sulfosalicylate and 1-hydroxy-4,7-disulfo-2-naphthoic acid. The greater stability of the disulfonate ligand complex can be seen as being due to the more exo-

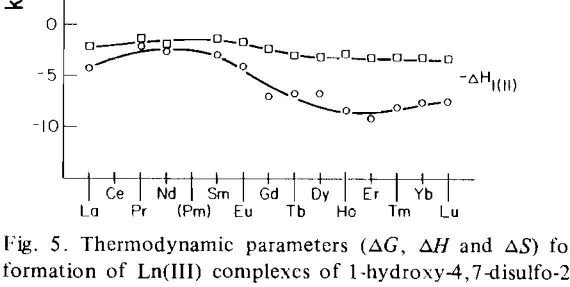

Fig. 5. Thermodynamic parameters (ΔG, ΔH and ΔS) for formation of Ln(III) complexes of 1-hydroxy-4,7-disulfo-2-naphthoic acid (○) and 5-sulfosalicylic acid (□).

ergic enthalpy as the entropies are roughly equivalent. This agrees with the interpretation of enhanced stabilization in this complex resulting from increased electronic charge polarization. Such an effect would not be expected to be reflected in the entropies but would make the enthalpy more negative for formation of the lanthanide-1-hydroxy-4,7-disulfo-2-naphthoate.

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References

1 G. R. Choppin, Q. Liu and C. Niu, *Lanthanide Actinide Res.*, in press.
2 L. H. J. Lajunen, *Finn. Chem. Lett.*, 36 (1976).
3 O. Mäkitie, L. H. J. Lajunen and P. Tamminen, *Finn. Chem. Lett.*, 3 (1976).
4 L. H. J. Lajunen, J. Eloranta and A. Kukkohovi, *Finn. Chem. Lett.*, 11 (1979).
5 'Beilsteins Handbuch der Organischen Chemie', 4. Auflage, XI, Berlin, 1928, p. 416.
6 H. Ruotsalainen, M. Lajunen and L. H. J. Lajunen, *Org. Magn. Reson.*, *21*, 154 (1983).
7 G. R. Choppin, P. A. Bertrand, Y. Hasegawa and E. N. Rizkalla, *Inorg. Chem.*, *21*, 3722 (1982).
8 A. Cassol, P. Di Bernardo, B. Portanova and L. Magon, *Gazz. Chim. Ital.*, *102*, 1118 (1972).
9 G. M. Navir and K. Chander, *J. Less-Common Met.*, *92*, 29 (1983).
10 L. H. J. Lajunen, E. Aitta and S. Parhi, *Talanta*, *28*, 277 (1981).
11 G. R. Choppin, *J. Less-Common Met.*, *112*, 193 (1985).
12 I. Fidelis and S. Siebierski, *J. Inorg. Nucl. Chem.*, *33*, 3191 (1971).
13 D. F. Peppard, C. A. A. Blomquist, E. P. Horwitz, S. Lewey and G. W. Mason, *J. Inorg. Nucl. Chem.*, *32*, 339 (1970).
14 G. Degisher and G. R. Choppin, *J. Inorg. Nucl. Chem.*, *34*, 2823 (1972).
15 G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, *22*, 97 (1961).
16 G. R. Choppin, A. Dadgar and R. Stampfli, *J. Inorg. Nucl. Chem.*, *35*, 875 (1973).
17 I. Dellien and L. A. Malmsten, *Acta Chem. Scand.*, *27*, 2877 (1973).