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Thermodynamics of Complexation of Lanthanides by 3- and 4-Hydroxybenzoic Acids

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Abstract

The thermodynamic parameters (log β_{101}, ΔH_{101}, and ΔS_{101}) for the formation of the 1:1 complexes between lanthanide cations and 3- and 4-hydroxybenzoate anions were determined by potentiometric and calorimetric titrations in aqueous solutions of 0.10 M ($NaClO_4$) ionic strength at 25 °C.

Introduction

A number of simple and substituted aliphatic carboxylic acids have been investigated as complexing ligands for trivalent lanthanide cations. In the past few years, such studies have been extended to benzoic acid [1] and substituted benzoic acids [2]. In this paper we report the results of potentiometric and calorimetric titration studies of lanthanides with 3- and 4-hydroxybenzoic acids. These thermodynamic data can be contrasted with that of lanthanide complexing with benzoate and 5-sulfosalicylate [3] ligands to clarify the factors involved in formation of the complexes of lanthanides with aromatic acids.

Experimental

Reagents

Stock solution of lanthanide perchlorates were prepared and analyzed as described previously [1]. Commercially available 3- and 4-hydroxybenzoic acids (Fluka) were used without further purification. The concentrations of aqueous solutions of the ligand acids were determined by titration with a standard sodium hydroxide solution. The buffer solutions of the ligands were prepared by dissolving the acids in known amounts of 1 M sodium hydroxide solution and adjusting the [L]:[HL] ratios with standardized perchloric acid solution followed by diluting to the desired concentrations of 0.03 to 0.04 M. This concentration ensured solubility of all the ligands. The stock solution of perchloric acid was prepared by dilution of concentrated perchloric acid (Baker) with deionized water and analyzed by titration with NaOH solution. The other chemicals were reagent grade. The metal and ligand solutions used in the titrations were adjusted to 0.10 M ionic strength with $NaClO_4$.

Procedures

The potentiometric measurements were performed with a Corning Model 130 pH meter and a combination electrode. The potentiometric system allowed pH readings to an accuracy of 0.001 pH units. The titrations were performed in the pH region between 4.0 and 5.0, where the liquid-junction potential due to the free hydrogen ions of the test solution is not significant [2]. The electrode was calibrated with solutions of known hydrogen ion concentration in 0.10 M ($NaClO_4$) ionic strength. All measured and calculated values were based on concentrations in that ionic medium.

The acidity constants, pK_a, of the carboxylic group of the ligands were measured in solutions without metal present. In these measurements the total concentration of the ligand acid (C_L) was kept constant and the total hydrogen ion concentration (C_H) was decreased by adding CO_2-free standard sodium hydroxide solution.

The stability constants of the lanthanide complexes were obtained by titration of lanthanide solutions with buffered ligand solutions. The concentration of lanthanide, C_M, varied from 0.005 to 0.02 M while that of the ligand, C_L, was about 0.04 M. The total hydrogen ion concentration in the titrant solution was varied between 0.01 and 0.015 M.

Calorimetric titrations were performed on a Peltier-cooled calorimeter with use of titration techniques described elsewhere [4, 5]. For a particular experiment, 50 ml of a lanthanide perchlorate solution ($0.015 < C_M < 0.020$ M) were titrated with 0.5 ml aliquots of the neutralized ligand solution ($C_L = 0.04$ M). The heats of dilution of the ligand and lanthanide concentrations were determined as described earlier [1].

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TABLE I. Sample Titration Data for the La(III)–3-Hydroxybenzoic and En(III)–4-Hydroxybenzoic Acid Systems (I = 0.10 M (NaClO$_4$); T = 25 °C)

(a) Potentiometric: La + 3-hydroxybenzoate

Titrant volume (ml)	10^5[H$^+$] (exp.) (M)	10^5[H$^+$] (calc.) (M)	10^3[M] (M)	10^3[L] (M)	$\bar{n}$ (calc.)
1.0	6.234	6.440	6.833	0.3727	0.023
1.5	6.483	6.538	6.693	0.5483	0.034
2.0	6.634	6.610	6.556	0.7185	0.047
2.5	6.726	6.668	6.423	0.8839	0.059
3.0	6.788	6.714	6.293	1.045	0.072
3.5	6.820	6.755	6.166	1.202	0.085
4.0	6.851	6.789	6.042	1.355	0.098
4.5	6.883	6.819	5.922	1.506	0.110
5.0	6.899	6.844	5.805	1.653	0.123
6.0	6.914	6.885	5.579	1.938	0.149
7.0	6,914	6.915	5.364	2.214	0.175
8.0	6.914	6.936	5.160	2.480	0.201
9.0	6.899	6.949	4.966	2.739	0.227
10.0	6.883	6.957	4.782	2.991	0.252

(b) Calorimetric: Er + 4-hydroxybenzoate [a]

Titrant volume (ml)	Q(corr.)[b] (mJ)	Q(calc.) (mJ)	10^2[M] (M)	10^3[L] (M)	−log [H$^+$]
0.5	149	156	1.709	0.1229	4.878
1.0	311	323	1.667	0.2569	5.100
1.5	477	489	1.626	0.3933	5.230
2.0	648	654	1.587	0.5313	5.319
2.5	820	817	1.548	0.6707	5.385
3.0	980	977	1.511	0.8113	5.438
3.5	1137	1135	1.475	0.9532	5.480
4.0	1287	1291	1.440	1.096	5.516
4.5	1452	1445	1.406	1.240	5.547
5.0	1608	1597	1.373	1.385	5.574
5.5	1756	1746	1.340	1.531	5.598
6.0	1881	1893	1.309	1.678	5.619
6.5	2043	2038	1.279	1.826	5.638
7.0	2186	2181	1.250	1.974	5.656
7.5	2321	2322	1.222	2.123	5.672
8.0	2460	2460	1.194	2.273	5.687
8.5	2593	2597	1.168	2.424	5.701
9.0	2729	2731	1.142	2.575	5.714
9.5	2864	2863	1.117	2.726	5.727
10.0	3001	2993	1.092	2.879	5.738

[a] Initial conditions: cup solution, volume 50.0 ml, C_M = 0.0175 M, C_H = 0.000048 M; titrant, C_L = 0.04054 M, C_H = 0.00054 M.
[b] Corrected for dilution effect.

Data Treatment

Since the protonation constants of the hydroxyl groups in 3- and 4-hydroxybenzoic acids are greater than 9 [6, 7] and the measurements were performed at pH $<$ 6, only the deprotonation of the carboxylate groups had to be taken into consideration.

The values of pK_a, log β_{101}, and ΔH_{101} were calculated with Simplex algorythm programs written by W. Cacheris. Deprotonation of the hydroxyl groups of the ligands, and hydrolysis of the lanthanide ions were neglected since the pH was always less than 6. In the analysis it was assumed that the pertinent equilibria were:

$$\mathrm{Ln}^{3+} + n\mathrm{HL}^- = \mathrm{Ln(HL)}_n{}^{3-n};\ \beta_{10n},\ n = 1 \text{ or } 2$$

$$\mathrm{H_2L} = \mathrm{HL}^- + \mathrm{H}^+;\ K_{a1}$$

In the calorimetric titrations the effect of the heats of protonation are small but were included in the calculations. For the protonation heats of 3- and 4-hydroxybenzoic acids the values −1.7 and −0.37 kJ/mol, respectively, were used [6].

TABLE II. Thermodynamic Parameters for Complexation of Lanthanides by 3- and 4-Hydroxybenzoic Acids ($I = 0.10$ M ($NaClO_4$); $T = 25$ °C)

Lanthanide ion	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ/mol)	ΔH_{101} (kJ/mol)	ΔS_{101} (J/mol K)
(a) Ln(III)–3-hydroxybenzoic acid systems				
La	1.76 ± 0.05	10.02 ± 0.28	8.60 ± 0.15	62.5
Pr	1.96 ± 0.04	11.16 ± 0.23		
Nd	2.08 ± 0.03	11.84 ± 0.17	7.51 ± 0.10	64.9
Sm	2.15 ± 0.03	12.24 ± 0.17	7.33 ± 0.14	65.6
Eu	2.13 ± 0.04	12.13 ± 0.23		
Gd	2.10 ± 0.03	11.96 ± 0.17	8.37 ± 0.08	68.2
Tb	1.95 ± 0.03	11.10 ± 0.17		
Dy	2.00 ± 0.04	11.39 ± 0.23	10.97 ± 0.08	75.0
Ho	1.96 ± 0.04	11.16 ± 0.23		
Er	1.90 ± 0.05	10.82 ± 0.28	11.96 ± 0.09	76.4
Tm	1.93 ± 0.06	10.99 ± 0.34		
Yb	1.93 ± 0.04	10.99 ± 0.23		
Lu	1.94 ± 0.05	11.05 ± 0.28		
(b) Ln(III)–4-hydroxybenzoic acid systems				
La	1.97 ± 0.03	11.22 ± 0.17	8.63 ± 0.08	66.6
Pr	2.23 ± 0.02	12.70 ± 0.11		
Nd	2.31 ± 0.03	13.15 ± 0.17	7.78 ± 0.08	70.2
Sm	2.42 ± 0.02	13.78 ± 0.11	7.57 ± 0.10	71.6
Eu	2.36 ± 0.02	13.44 ± 0.11		
Gd	2.27 ± 0.02	12.93 ± 0.11	8.49 ± 0.09	71.8
Tb	2.15 ± 0.02	12.24 ± 0.11		
Dy	2.13 ± 0.02	12.13 ± 0.11	12.25 ± 0.09	81.8
Ho	2.06 ± 0.03	11.73 ± 0.17		
Er	2.05 ± 0.03	11.67 ± 0.17	12.98 ± 0.09	82.7
Tm	2.08 ± 0.03	11.84 ± 0.17		
Yb	2.28 ± 0.03	11.98 ± 0.17		
Lu	2.10 ± 0.04	11.96 ± 0.23		

Results and Discussion

Typical sets of potentiometric and calorimetric data are listed in Table I. To reflect the validity of the final constants, each experimental [H^+] and Q (heat change) are compared with the values calculated for that titration point with those constants. The thermodynamic parameters ($\log \beta_{101}$, ΔG_{101}, ΔH_{101}, and ΔS_{101}) are given in Table II. The standard deviations in individual titrations for K_{a1}, $\log \beta_{101}$, and ΔH_{101} were estimated to be 0.0001–0.002, 0.002–0.005, and 0.02–0.07, respectively. However, the errors given in Table II are based on the agreement in repetitive titrations since these are larger than the estimated standard deviations. Both potentiometric and calorimetric titrations gave evidence of the formation of the second complex, LnL_2^+, but no values of $\log \beta_{102}$ or ΔH_{102} are reported as the maximum $\bar{n}$ values were too small to allow valid estimates. The protonation constants were measured to be 4.02 ± 0.01 (3-hydroxybenzoic acid) and 4.38 ± 0.01 (4-hydroxybenzoic acid) which agree well with the values reported by Ishimitsu *et al.* [6] when the difference in the ionic strength is taken into account.

Figure 1 shows the relationship between the value of $\log \beta_{101}$ for a number of Sm(III) complexes with alkyl and aryl monocarboxylate ligands and the acidity, pK_{a1}, of the ligand acid. The values for all the ligands except the salicylate fall on a common line. The higher value for the salicylate complexing reflects chelate stabilization involving the carboxylate and the ortho phenol groups. The common relationship of the $\log \beta_{101}$ with the carboxylic acid pK_a values of the other ligands indicates that the lanthanides are bound only via the carboxylate group and the bonding is ionic since it is dependent on the effective ligand negative charge as measured by the pK_a value.

In Fig. 2, the thermodynamic parameters of complexation of the lanthanides with *o*-, *m*-, and *p*-hydroxybenzoate ligands are compared. These curves show that the chelation with the *ortho*-substituted ligand provides added stabilization through the enthalpy of complexation. The entropy of complexation of the *ortho*-substituted ligand is less positive

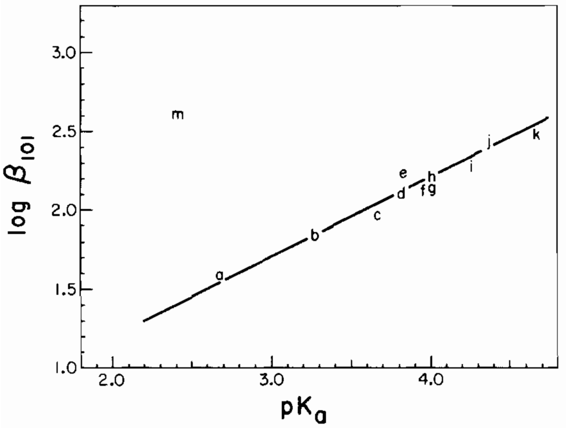

Fig. 1. Relationship between the stability constant, log β_{101}, for formation of SmL^{2+} and the acid constant, pK_a, of HL: a = iodoacetate [7]; b = 3-nitrobenzoate [2]; c = 3-fluorobenzoate [2]; d = *o*-methoxybenzoate [8]; e = *m*-methoxybenzoate [8]; f = 4-fluorobenzoate [2]; g = 3-hydroxybenzoate (p.w.); h = benzoate [1]; i = *p*-methoxybenzoate [8]; j = 4-hydroxybenzoate (p.w.); k = propionate [7]; m = 5-sulfosalicylate [3].

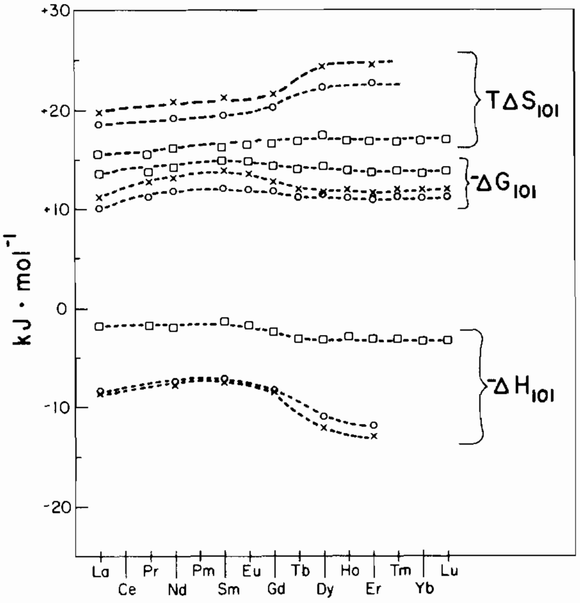

Fig. 2. Thermodynamic parameters ($-\Delta G_{101}$, $-\Delta H_{101}$, and $T(\Delta S_{101})$) for formation of LnL^{2+} complexes: (○) 3-hydroxybenzoic acid, (×) 4-hydroxybenzoic acid, (□) 5-sulfosalicylic acid.

than for the complexation of the monodentate *meta*- and *para*-substituted ligands. This difference reflects the loss of entropy upon chelation.

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