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THE NATURE OF CALCIUM AND THORIUM COMPLEXATION BY HALATE LIGANDS

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The thermodynamics of complexation of Th^{+4} and Ca^{+2} ions with chlorate, bromate, and iodate ligands were studied using solvent extraction and calorimetric techniques. The measurements were obtained at 1.00 M (NaClO_4) ionic strength and 25°C. The results are compared to the values for complexation of Eu^{+3} by the same ligands and are interpreted to reflect outer sphere complexation for the chlorate complexes, an inner sphere complexation for the iodates and mixed behaviour for the bromates.

Keywords: Calcium, thorium, halate, stability constants

INTRODUCTION

Outer sphere complexation in which a ligand is not bound to a cation directly but through an intervening water of hydration is considered an intermediate step in the mechanism by which inner sphere complexation (*i.e.*, direct metal ligand bonding) occurs. In the case of weak base ligands, however, the complexation may stop with outer sphere complexation, particularly in the case of the 1:1 species. For hard acid cations and hard base anions, outer sphere complexation is associated most frequently with negative values for both the enthalpy and the entropy change for complexation while inner sphere complexation, at least for simpler ligands, is usually characterized by positive values of these parameters.^{1,2}

We have reported earlier³ on the complexation of Eu^{+3} and of uranyl, $\text{UO}_2^{+2,4}$ by halate ligands. For both cations, the data are consistent with complexation that is outer sphere with chlorate, inner sphere with iodate, and mixed with bromate. In the present work we report the extension of these studies with the halate ligands to complexation with Ca^{+2} and Th^{+4} . These cations have similar ionic radii to trivalent lanthanides and, like the latter, form bonds which are predominantly ionic. Comparison of their data with that of Eu^{+3} could be expected to provide insight into the relationship between cation charge density of hard acid cations and the nature (inner/outer sphere) of the complexes.

EXPERIMENTAL

Reagents

Stock solutions of approximately 0.5 M were prepared from calcium (Alpha) and thorium (Pfalz and Bauer) perchlorates by dissolving the salts in water, acidifying to the desired pH (4 for the calcium solution and 2 for the thorium solution). The solutions were standardized by standard procedures.⁵ Sodium iodate (Mallinckrodt), sodium bromate (Baker) and sodium chlorate (Baker) solutions were prepared from

the anhydrous grade reagents without further purification. All solutions were adjusted to 1.00 M ionic strength with NaClO_4 .

Stock solution of the extractants di(2-ethylhexyl)phosphoric acid, HDEHP (Pfaltz and Bauer), and thenoyltrifluoroacetone, TTA (Aldrich), were prepared by dissolving the appropriate weight of HDEHP in toluene and of TTA in benzene. HDEHP was purified by the method of Peppard *et al.*⁶, and TTA by vacuum sublimation. The purified TTA was stored in darkness under vacuum (m.p. 42.8°C) prior to use.

^{230}Th and ^{45}Ca were obtained from the Oak Ridge National Laboratory and New England Nuclear Company, respectively. The thorium was purified by dissolution of the ThO_2 in 7.0 M HNO_3 and sorption of the thorium on a column of anion exchange resin (Dowex 1-X8 in nitrate form). The thorium was eluted with 0.01 M HClO_4 and its radiochemical purity confirmed by multichannel analysis (Canberra) of the alpha spectrum using a Si detector and of the gamma spectrum using a Ge(Li) detector. The calcium tracer was converted from the chloride salt to the perchlorate salt by repeated digestion with 0.10 M HClO_4 .

An extraction cocktail for counting alpha decay by liquid scintillation was prepared by dissolving 6.45 g of HDEHP and 6.00 g of PPO (2,5-diphenyloxazole) per litre of toluene solvent (which had been purified by passage through an alumina column). The beta decay rate of ^{45}Ca was counted using the scintillation cocktail prepared by dissolving 32.23 g of HDEHP and 6.00 g of PPO per litre of purified toluene. The calcium was extracted from the aqueous phase into the cocktail after adjustment of the solution to pH 7.

Measurements

The solvent extraction measurements followed procedures described in a previous publication.⁴ Correction for pH changes in the aqueous phase were made when necessary.

Calorimetric measurements were made with a semi-adiabatic Peltier-cooled calorimeter interfaced to a microcomputer.⁷ In all cases, ligand solutions were titrated into metal solutions (50 cm³) of the same ionic strength (1.00 M NaClO_4). The temperature changes were monitored with a 20 k Ω thermistor. Electrical calibrations were made automatically after each sequence of four additions of titrant. Complexation heats for thorium solutions were obtained with solutions adjusted to pH 2 to minimize metal hydrolysis.

RESULTS AND DISCUSSION

The protonation enthalpy of the iodate ion was measured by calorimetric titration of a solution of the ligand salt with perchloric acid. The value obtained, ΔH_{011} , was $3.7 \pm 0.2 \text{ kJ mol}^{-1}$. Enthalpies of protonation of the chlorate and bromate anions were not determined since their acids were fully ionized under the experimental conditions. The acid constant values of reference 3 were used in this study.

Extraction experiments of Ca in the absence of halate ions showed linear slopes with third power dependency on the HDEHP concentration. This was in agreement with an earlier study and confirmed the extraction of $\text{HCa}(\text{DEHP})_3$.⁸ The absence of such a species as $\text{Ca}(\text{DEHP})(\text{ClO}_4)$ was also confirmed by the slope of the extraction. For Th, the extraction in the absence of halates had a fourth power

dependence on TTA, indicating extraction of $\text{Th}(\text{TTA})_4$ as reported previously⁹ and eliminating the possibility of mixed $\text{TTA} + \text{ClO}_4$ extracted species. Polynuclear extracted species were not considered as tracer metal concentrations were used. We assume no extraction of the halic acids as they are so strong. Weak organic acids can be extracted but these strong inorganic acids are too hydrophilic to have significant solubility in the organic solvents.¹⁰

The stability constants for the metal complexes were calculated by a linear regression program from the best fit to the expression

$$1/D = 1/D_0(1 + \beta_{101}[\text{X}^-])$$

where X^- is the halate ion.¹⁰ D is the distribution of the metal between the organic and the aqueous phase in the presence of X , while D_0 is the distribution in the absence of X . Sample sets of extraction data are listed in Table I. The values for ThX^{+3} were corrected as described elsewhere¹¹ for the small degree of hydrolysis of the Th^{+4} at the pH of these experiments.

TABLE I
Solvent extraction data, $T = 298 \text{ K}$; $I = 1.00 \text{ M}$ (NaClO_4).

[X^-], M	Activity (cpm)		pH	$1/D_{\text{corr}}^b$
	Organic ^a	Aqueous		
<i>A. $\text{Ca}^{+2} + \text{BrO}_3^-$</i>				
0.000	4606	4675	2.878	0.563
	4662	4474		
0.20	4076	4270	2.884	0.612
	4150	4316		
0.40	5614	3853	3.022	0.759
	5614	3852		
0.60	4131	2736	2.983	0.843
	4230	3885		
0.80	4388	3828	3.013	0.917
	4305	3683		
$\beta_{101} = 0.85 \pm 0.12$				
<i>B. $\text{Th}^{+4} + \text{ClO}_3^-$</i>				
0.00	9455	775	2.060	0.1399
	9983	791		
0.20	10152	1025	2.061	0.1771
	10430	1054		
0.60	9601	1334	2.062	0.2498
	9218	1347		
0.80	10056	1612	2.061	0.2762
	10360	1604		
1.00	9063	1763	2.061	0.3382
	9411	1799		
$\beta_{101} = 1.37 \pm 0.30$				

^a 0.05 M HDEHP in toluene for Ca and 0.006 M TTA in benzene for Th. ^b D for Th corrected for hydrolysis;⁸ D values were corrected in all systems to a constant pH value.

The enthalpies of complexation were calculated using a standard program.¹² The observed heats were corrected for the heats of dilution and fitted to the general equation (1),

$$\Sigma Q_{\text{cor}} = (\Delta n_{\text{HL}}) \cdot \Delta H_{011} + (\Delta n_{\text{ML}}) \cdot \Delta H_{101} \quad (1)$$

where Δn_x is the change of moles of the species x with each titrant addition. Sample sets for calcium and thorium calorimetric measurements are given in Table II. A summary of the thermodynamic parameters is listed in Table III. These estimated

TABLE II
Calorimetric titration data, $T=298\text{ K}$, $I=1.00\text{ M}$ (NaClO_4).

Vol. cm^3	$-\Sigma Q_{\text{cor}}$ mJ	$[\text{M}^{+2}]$ mM	$[\text{L}^-]$ mM	$[\text{H}^+]$ nM	n
<i>A. $\text{Ca}^{+2} + \text{IO}_3^-$^a</i>					
0.10	7.8	86.8	0.15	0.020	0.0005
0.20	18.1	86.6	0.30	0.020	0.0010
0.30	27.2	86.4	0.45	0.020	0.0015
0.50	40.5	85.9	0.75	0.020	0.0025
0.70	28.0	85.5	1.05	0.020	0.0035
0.90	28.2	85.1	1.35	0.020	0.0044
1.00	36.9	84.9	1.50	0.020	0.0049
1.10	48.1	84.7	1.64	0.021	0.0054
1.20	62.4	84.5	1.79	0.021	0.0059
1.30	67.4	84.3	1.94	0.021	0.0064
1.40	74.9	84.1	2.08	0.021	0.0068
1.50	84.1	83.9	2.23	0.021	0.0073
1.60	97.8	83.7	2.37	0.021	0.0078
1.70	106.5	83.5	2.52	0.021	0.0082
1.80	111.8	83.3	2.66	0.021	0.0087
1.90	107.0	83.1	2.81	0.021	0.0092
2.00	112.0	82.9	2.95	0.021	0.0096
				$\Delta H_{101} = 2.6 \pm 0.3 \text{ kJ mol}^{-1}$	
<i>B. $\text{Th}^{+4} + \text{IO}_3^-$^b</i>					
0.10	47.8	10.16	0.05	10.01	0.014
0.20	97.1	9.99	0.09	10.02	0.029
0.30	148.6	9.83	0.14	10.03	0.043
0.40	199.3	9.67	0.19	10.05	0.056
0.50	251.0	9.51	0.24	10.06	0.070
0.60	294.8	9.35	0.30	10.07	0.084
0.70	341.4	9.19	0.35	10.08	0.098
0.80	379.1	9.04	0.40	10.09	0.111
0.90	417.2	8.88	0.46	10.10	0.125
1.00	461.5	8.73	0.51	10.11	0.138
				$\Delta H_{101} = 8.8 \pm 0.3 \text{ kJ mol}^{-1}$	

^aFor Ca titration: cup contents; 50.0 cm^3 of 87.023 mM of $[\text{Ca}^{+2}]$ and $\text{pH } 4.70$; burette contents; 97.733 mM sodium iodate and $\text{pH } 4.24$. ^bFor Th titration: cup contents; 50.0 cm^3 of 10.33 mM of $[\text{Th}^{+4}]$ and $\text{pH } 2.00$; burette contents; 99.7 mM sodium iodate and $\text{pH } 2.00$.

error limits for the stability constants are the compounded errors from the uncertainties in pH, sampling, counting statistics, *etc.*, based on a 95% confidence limit provided by the T-test of the best experimental fit. The error limits for the calorimetric data are the average deviations from the respective runs.

Although the ionic strength was maintained constant, the ionic composition was varied as halate replaced perchlorate. The activity coefficient (γ_{\pm}) of 1.0 M NaClO₄ is 0.63, of 1.0 M NaClO₃, 0.59, and of NaBrO₃ 1.0 M, 0.53.¹³ The effects of changes in ionic composition have been studied in the Eu⁺³/NO₃⁻ system.¹⁴ Using the same approach, we estimate, for example, that log β_1 of ThClO₃⁺³, would be 0.26 as compared to 0.14 reported in Table III. This change would decrease ΔH_{101} slightly but cause little difference in ΔS_{101} . In all systems, the corrections would almost fall within the listed error limits and would not change the interpretation of the values in Table III.

There are only a few reports on these systems in the literature. A value of log β_{101} = 0.89 for I = 0 is recommended by Smith and Martell¹⁵ for CaIO₃⁺ formation which is consistent with our value of 0.52 at I = 1.0 M. For thorium, values at I = 0.5 M of log β_{101} = 0.26, 0.81, and 2.88 are reported¹⁶ for formation of the chlorate, bromate, and iodate, respectively. Again, given the difference in ionic strength, the agreement with our values is satisfactory. Recently, the complexation of Th(IO₃)_n⁴⁻ⁿ (n = 1–3) was studied at I = 0.5 M by calorimetry.¹⁷ Using log β_{101} = 2.88, values of ΔH_{101} = 3.3 ± 0.2 kJ mol⁻¹ and ΔS_{101} = 66 ± 1 J K⁻¹ mol⁻¹ were obtained, values which are not inconsistent with ours, given the difference in ionic strength.

The stability of the halate complexes of both Ca⁺² and Th⁺⁴ ions show the same pattern as for Eu⁺³ complexation, *i.e.*, an increase from chlorate to bromate to iodate.

TABLE III
Thermodynamic parameters for complexation of Ca⁺² and Th⁺⁴ by halate anions, T = 298 K; I = 1.00 M (NaClO₄).

Ion	log β_{101}	$-\Delta G_{101}$ (kJ mol ⁻¹)	ΔH_{101} (kJ mol ⁻¹)	ΔS_{101} (J K ⁻¹ mol ⁻¹)
<i>A. Chlorate (pK_a = -2.50)</i>				
Ca	-0.52 ± 0.11	-2.98 ± 0.63	-2.3 ± 0.4	-18 ± 3
Eu*	0.04 ± 0.07	0.25 ± 0.40	-6.3 ± 1.7	-20 ± 7
Th	0.14 ± 0.08	0.78 ± 0.46	2.4 ± 0.8	11 ± 3
<i>B. Bromate (pK_a = -2.05)</i>				
Ca	-0.07 ± 0.06	-0.40 ± 0.34	-1.2 ± 0.5	-5 ± 2
Eu*	0.59 ± 0.04	3.39 ± 0.25	-2.5 ± 1.3	3 ± 5
Th	0.63 ± 0.06	3.61 ± 0.34	2.5 ± 0.6	20 ± 2
<i>C. Iodates (pK_a = +0.95)</i>				
Ca	0.52 ± 0.05	2.96 ± 0.29	2.6 ± 0.3	19 ± 2
Eu*	1.14 ± 0.07	6.53 ± 0.42	11.3 ± 0.8	59 ± 6
Th	2.49 ± 0.02	14.21 ± 0.11	6.5 ± 0.4	70 ± 1

* Data for Eu is for 0.1 M ionic strength.

This order parallels that of the pK_a values, as expected for systems dominated by electrostatic interactions. Also, for a particular halate ion, the values of $\log \beta_{101}$ increase with the cationic charge, further reflecting the ionic nature of these complexes.

The enthalpy and entropy changes are the result of the disruption of the solvation shell and of the combination of the metal and ligand. The association of the metal and the ligand ions results in negative enthalpy and entropy changes while dehydration produces positive changes in these terms. In the case of inner sphere complexation of 1:1 species of hard acid-hard base systems, the hydration disruption is often more important, causing the net entropy and enthalpy changes to be positive. In outer sphere complexation, the metal-ligand combination and the dehydration effects are both smaller, resulting in small net ΔH and ΔS values, which are often, but not always, negative. Based on these criteria, the complexation of Eu^{+3} by chlorate was assigned an outer sphere nature. The values for formation of CaClO_3^+ also indicate a dominant outer sphere nature. Formation of MnClO_3^+ , CoClO_3^+ , NiClO_3^+ , and ZnClO_3^+ is characterized by small values of $\log \beta_{101}$ and negative values of ΔS_{101} was the basis for the assignment of outer sphere character to these transition metal chlorate complexes.¹⁸

A large positive ΔS_{101} for EuIO_3^{+2} formation provided the basis of assignment of an inner sphere nature. The large, positive value of ΔS_{101} for ThIO_3^{+3} formation allows a similar assignment of inner sphere to this complex. The small values of $\log \beta_{101}$ and ΔS_{101} for ThClO_3^{+3} formation probably reflects a primarily outer sphere nature although the values are not inconsistent with a small degree of inner sphere complexation. The bromate complexes have values of $\log \beta_{101}$ and ΔS_{101} which are consistent with a mixture of inner + outer sphere complexation. There does seem to be an effect of cation charge on the nature of the halate complexes since, relative to Eu^{+3} , Th^{+4} seems to have more inner sphere character in the chlorate and bromate complexes while Ca^{+2} may have more outer sphere nature in the bromate and even

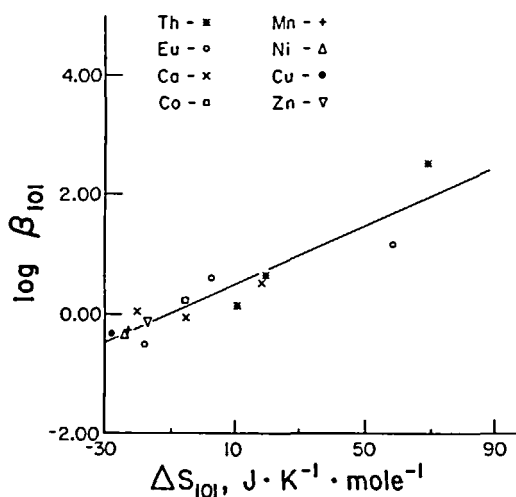


FIGURE 1 Correlation of $\log \beta_{101}$ and ΔS_{101} for halate complexation.

some in the iodate complex. However, the effect of cation charge density does not seem to be as strong as that due to the differences in ligand basicity (as reflected by the pK_a values).

It has been proposed¹⁸ that $\log \beta_{101}$ and ΔS_{101} should show a correlation if the interaction is strongly electrostatic. This proposal is based on the relationships from the Born and Bjerrum electrostatic theories,¹⁹⁻²¹

$$-\Delta G^\circ = |Z_c Z_r| / rD \quad (2)$$

$$\Delta S^\circ = \frac{-\delta \Delta G^\circ}{\delta T} = \frac{|Z_c Z_r|}{rD} \left(\frac{\delta \ln D}{\delta T} \right)_P \quad (3)$$

where Z_c and Z_r are the cationic and anionic charges, respectively, r is the interionic distance of closest approach and D is the dielectric constant. From equations (2) and (3), for electrostatic interactions we would expect a plot of $\log \beta_{101}$ vs ΔS_{101} to have a slope of 0.026 (22). Figure 1 shows such a plot which includes the values from Table III as well as the values for chlorate complexes of the divalent cation complexes in reference 18. The slope of the linear least squares correlation has a value of 0.024. The correlation in Figure 1 shows no variation in slope between the strongly outer sphere chlorate complexes and those of the strongly inner sphere iodates. This plot also would seem to support an intermediate character for CaIO_3^+ .

The conclusions of this study are that outer sphere complexation is favored by very weak basicity of the ligands and low cation charge density but the latter is the more significant effect.

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