Thermodynamics of the Complex Formation between Thorium(IV) and some Polydentate Ligands in Aqueous Solution

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The changes in free energy, enthalpy, and entropy for the formation of thorium(IV)–oxydiacetate, –iminodiacetate, –thiodiacetate, and –succinate complexes have been determined by potentiometric and calorimetric titrations at 25 °C in aqueous 1 mol dm^{-3} sodium perchlorate. All the ligands form 1 : 1 chelate complexes with the thorium(IV) ion the stability of which is dependent on both the chelate ring dimensions and the nature of the donor group in the chain. The order of the relative stabilities (iminodiacetate > oxydiacetate > thiodiacetate > succinate) is mainly dependent on the reaction enthalpies, since the ΔS° values are close to each other. In the thorium(IV)–oxydiacetate system the maximum number of three ligands for every metal ion was reached. Because of precipitation of solid compounds in the other systems, it was only possible to define complexes with a lower number of co-ordinated ligands: two for succinate and thiodiacetate, and one for iminodiacetate. Owing to the lower stability of the chelate ring of thiodiacetate and succinate complexes and the high basicity of the amino-group of iminodiacetate, these ligands form also unchelated protonated complexes.

In recent years the complexation in aqueous solution of actinide ions by charged oxygen donors such as mono-, di-, and poly-carboxylate anions has been extensively studied.[1] The principal aim of most of these investigations was the determination of the stoicheiometric composition and stability (*i.e.* ΔG° of formation) of the complex species in solution. Recently, some papers containing more complete data (ΔG°, ΔH°, and ΔS°) on the formation of actinide complexes with these ligands have been published.[2–5]

As far as the thorium(IV) ion complexes are concerned, at the present time only the free energies, enthalpies, and entropies of formation of the acetate, monochloroacetate, glycolate, thioglycolate, and malonate complexes have been reported.[6–9]

In this paper, we report an extension of these studies to the dicarboxylate ligands (L): succinate (succ), oxydiacetate (oda), *N*-iminodiacetate (ida), and thiodiacetate (tda). The aim of the present work is to elucidate the role of ring size and donor group in the formation of thorium(IV) chelate complexes.

Stability constants and enthalpies of complex formation have been determined using potentiometric and calorimetric techniques respectively.

Experimental

Reagents.—Solutions of thorium(IV) perchlorate, sodium hydroxide, and sodium perchlorate were obtained and standardized as described elsewhere.[2,10] The dicarboxylic acids were purified according to reported methods [11] and their purity checked by alkalimetric titrations. All the solutions were prepared in doubly distilled water.

Apparatus.—E.m.f. measurements were carried out with a Radiometer model 64 pH meter using a four-neck jacketed glass cell through which water at 25.0 ± 0.1 °C was circulated by a constant-temperature bath. The titration vessel was set with a selected glass electrode (Jena Glass, Thalamide type) and a double junction Ag–AgCl reference electrode (Metrohom EA 440).

The calorimetric measurements were carried out with a titration calorimeter LKB 8700-2 at 25 °C in a room thermostatted at 25 ± 1 °C.

The ionic strength of all the solutions was maintained at 1 mol dm^{-3} using sodium perchlorate as neutral salt.

Methods.—The e.m.f. of the titration cell was, as usual, described by $E = E^\circ - 59.16 \log[H^+] + E_j$, where E° is the cell constant and E_j the liquid junction potential. For each experiment both E° and E_j were determined by e.m.f. values obtained when a known excess of perchloric acid in the solution containing the metal perchlorate was partially neutralized by standard carbonate-free sodium hydroxide. The base was added very slowly to avoid local formation of hydroxo-complexes and additions stopped at $[H^+]$ values where the thorium(IV) ions did not appreciably hydrolyze. Immediately after the determination of E° and E_j, the resulting solution containing known metal- and hydrogen-ion concentrations (in the range 5×10^{-3}—3×10^{-2} and 5×10^{-3}—2×10^{-2} mol dm^{-3} respectively) was used as a starting solution in a potentiometric titration thus avoiding the errors arising from the washing and reassembly of the cell. Other details on the e.m.f. measurements are given in ref. 7.

The experimental procedure of the calorimetric measurements was the same as described before.[2]

For each system some potentiometric and calorimetric titrations with buffer solutions of the ligands having different C_{H_2L}/C_{Na_2L} ratios were carried out in order to change adequately the concentration of the complexing species and the medium acidity.

The thermodynamic functions relative to the formation of proton-ligand complexes were those used in refs. 4 and 5.

The composition of the thorium(IV) complexes, their stability constants, and enthalpies of formation were determined using the generalized least-squares programs LETAGROP VRID and MINIQUAD [12,13] for the potentiometric

Table. Stability constants and free energy, enthalpy, and entropy changes for the formation of the thorium(IV) complexes at 25 °C and $I = 1.00$ mol dm^{-3} [Na(ClO$_4$)]

Reaction	log K	$-\Delta G^\circ$/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
(*a*) Th^{4+}-oda				
$M + L \rightleftharpoons ML$	8.15 ± 0.08	46.52	8.37 ± 0.50	184
$ML + L \rightleftharpoons ML_2$	6.67 ± 0.13	38.07	—11.46 ± 0.63	89
$ML_2 + L \rightleftharpoons ML_3$	3.34 ± 0.10	19.07	35.90 ± 0.63	184
(*b*) Th^{4+}-ida				
$M + L \rightleftharpoons ML$	9.69 ± 0.03	55.31	6.5 ± 1.0	207
$M + HL \rightleftharpoons MHL$	2.91 ± 0.03	16.61	7.41 ± 0.88	81
(*c*) Th^{4+}-tda				
$M + L \rightleftharpoons ML$	5.60 ± 0.03	31.97	20.5 ± 1.1	176
$M + HL \rightleftharpoons MHL$	3.29 ± 0.16	18.79	12.4 ± 1.5	105
$ML + L \rightleftharpoons ML_2$	4.25 ± 0.15	24.27	14.9 ± 1.3	131
(*d*) Th^{4+}-succ				
$M + L \rightleftharpoons ML$	6.44 ± 0.03	36.78	18.6 ± 1.1	186
$M + HL \rightleftharpoons MHL$	3.60 ± 0.03	20.54	8.53 ± 0.38	97
$M + HL + L \rightleftharpoons MHL_2$	8.94 ± 0.09	51.04	24.7 ± 2.5	254
(*e*) Th^{4+}-malonate *				
$M + L \rightleftharpoons ML$	7.47	42.64	11.88	183
$ML + L \rightleftharpoons ML_2$	5.32	30.33	8.49	130
$ML_2 + L \rightleftharpoons ML_3$	3.49	19.92	4.60	82

* Data from ref. 7.

data treatment and LETAGROP KALLE[14] for the calorimetric one.

Results and Discussion

As mentioned above, our intention was to obtain the stability constants of all the complexes by potentiometric determination of the competitive H$^+$ ion concentration. In studying the thorium(IV)-oxydiacetate system, we noted that, for $C_L/C_M < 1$ and $C_H \leqslant 0.05$ mol dm^{-3}, no changes in hydrogen ion concentration were obtained in titrations of Th^{IV} with Na$_2$(oda) solutions, apart from those from dilution. This clearly indicated that the metal–ligand complex was noticeably strong relative to the proton-ligand complex and made the competition method unsuitable for the first stability constant, β_1, determination. Henceforth we increased the competing power of H$^+$ by increasing its concentration and, because accurate potentiometric measurements cannot be carried out at such high hydrogen ion concentrations[15] ($C_H > 0.1$ mol dm^{-3}), we limited our investigations to calorimetric measurements. The results of some of the calorimetric titrations are given in the Figure as Δh_V, the total heat change per mol of metal after addition of V cm^3 of titrant, *versus* the ligand-to-metal mol ratio, C_L/C_M. The Δh_V sum is extended over all heat effects other than those due to protonation and dilution. As observed, the experimental values for titrations carried out on solutions containing low mineral acid concentration superimpose only for $C_L/C_M < 0.5$. At higher values of this ratio the experimental points for the titration carried out with the sodium salt of the ligand (●, Figure) stay below those obtained using oxydiacetic acid as titrant (△, Figure). Such a trend is explicable by admitting in this last case formation of a lower quantity of the second complex whose formation enthalpy is significantly exothermic (see Table). This detail and the above observations on the completeness of the reaction for $C_L/C_M < 1$ indicate that although the ligand completely reacts to give products, their relative quantities are strictly dependent upon the medium acidity. As C_H increases (□ < ○ < ▽, Figure) the net reaction heat, and consequently the number of moles of complexes, progressively decreases owing to the competition between H$^+$ and Th^{4+}. The reliability of the values of ΔH° and K obtained from the least-squares fit of data is well illustrated by the agreement between the full-drawn calculated curves and experimental values.

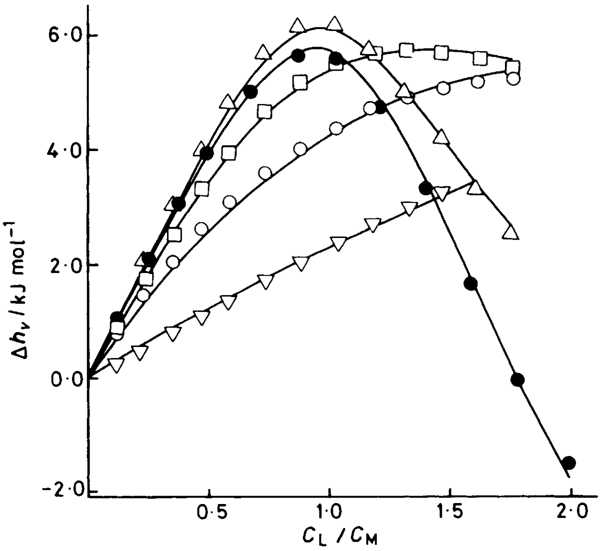

Figure. The total molar heat change, Δh_V, as a function of C_L/C_M for the thorium–oxydiacetate system. The initial metal ion concentration was 10.13 × 10^{-3} mol dm^{-3} in all the titrations. The concentration of the titrand was 0.1058 mol dm^{-3} in Na$_2$(oda) (●) and 0.1008 mol dm^{-3} in H$_2$oda (△, □, ○, and ▽). The initial concentrations of perchloric acid (in 10^{-3} mol dm^{-3}) were 15.15 (●), 20.54 (△), 188.9 (□), 385.1 (○), and 959.5 (▽). The full-drawn curves have been computed from the experimentally determined stability constants and enthalpy changes

For the systems thorium(IV)–iminodiacetate, –thiodiacetate, and –succinate it was not possible to extend the titrations to $\bar{n}$ (mean number of co-ordinated ligands) higher than 0.6, 1.2, and 1.4 respectively. The formation of slightly soluble precipitates made it impossible (for these systems) to calculate the free energies, enthalpies, and entropies for complexes with more than one ligand for the iminodiacetate and two for the thiodiacetate and succinate systems. The stoicheiometric composition of the solid phase was well defined by elemental analysis for the thiodiacetate system {[Th(tda)$_2$]·H$_2$O} but not for the other two.

In the Table the thermodynamic parameters determined in the course of the present study are listed. The quoted errors correspond to three standard deviations. For the sake of comparison in the Table the values relative to the formation of the thorium(IV)–malonate complexes taken from ref. 7 are also reported.

The Table reveals that the favourable $\Delta G^\ominus$ for the formation of complexes results principally from positive $\Delta S^\ominus$ values; $\Delta H^\ominus$ is seen to be in all cases unfavourable, except for the formation of the complex [Th(oda)$_2$].

The high values of the stability constants and entropy changes relative to the formation of the four 1 : 1 complexes indicate the formation of chelate species. On account of the ligand conformation, one must admit that oda, ida, and tda form two five-membered chelate rings *via* the carboxylate groups and the O, N, or S atom in the chain. To our knowledge a chelate complex containing a ' hard ' ion involved in an eight-membered ring has never previously been observed. Although $\Delta H^\ominus$ seems to have little effect upon $\Delta G^\ominus$, the different stabilities of these 1 : 1 complexes are mainly due to this term, since the $\Delta S^\ominus$ values are similar to each other. The ligands oda, ida, and tda are also similar; therefore it seems correct to ascribe the different $\Delta H^\ominus$ to the different donor abilities of the atoms in the chain. This trend, also observed for the corresponding complexes of uranyl ion,[5] supports the view that the relative affinity of the donor group toward a ' hard ' ion follows the order $-\mathrm{NH}- > -\mathrm{O}- > -\mathrm{S}-$. Furthermore, the values in the Table also suggest that the lower stability of the thorium monosuccinate complex compared with that of the monomalonate is due only to the higher unfavourable enthalpy term as a probable consequence of the greater strain present in the seven-membered chelate ring of the succinate complex.

The weaker the chelate the stronger is the tendency for formation of mixed complexes; for this reason the thiodiacetate and succinate ions form protonated complexes. Iminodiacetate is the strongest chelating agent among those considered and yet forms a protonated complex, but in this case the protonation of the highly basic amino-group in the chain ($\mathrm{p}K_a$ = 9.31) rather than that of the terminal carboxylate group provokes the disruption of the chelate ring.

The stability constants, entropy, and enthalpy values for the formation of [Th(HL)] complexes agree with those expected for monocarboxylate ions of the same basicity.[6,8,9]

The $\Delta H^\ominus$ and $\Delta S^\ominus$ values for the formation of the oxydiacetate complexes follow a different trend from that of malonate for which a regular decrease on increasing the number of co-ordinated ligands was observed. The abrupt increase of $\Delta H_3^\ominus$ and $\Delta S_3^\ominus$ relative to the formation of the oxydiacetate complex clearly indicates a drastic rearrangement of the ligand molecules around the metal ion. Structural evidence may help to elucidate the relative disposition of the oxydiacetate ions in the second and third complexation steps but unfortunately at present none is available.

Finally, a comparison between the stability constants reported here and those of the uranyl(VI) ion with the same ligands[4,5] reveals that the increased charge of the acceptor gives rise to a diminution of the difference among the complex stabilities, so denoting a charge levelling effect.

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