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Thermodynamic Properties of Actinide Complexes. Part VI. Thorium(IV)–Monochloroacetate System

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As has been stressed in the previous paper in this series [1–5], the changes of free energy, enthalpy and entropy for the complex formation between UO_2^{2+} and Th^{4+} ions and carboxylate ligands in aqueous solution are affected both by the geometrical requirements of the ligands and the metal charge. Moreover, while the monocarboxylate system of UO_2^{2+} shows a decrease of ΔH_j^o and ΔS_j^o at each consecutive step, as expected for hard–hard interactions [6], the thorium(IV)–acetate system exhibits a reversal on the formation of the third complex [2]. This reversal has been interpreted as a change of coordination taking place at this particular step [2].

In an attempt to obtain more information regarding structural changes at the formation of thorium complexes, the investigations were extended to other carboxylate systems. The monochloroacetate system seemed suitable as this ligand is structurally similar to acetate but differs by being much less basic.

This paper deals with the determination of enthalpy changes, ΔH_j^o, at the formation of thorium complexes with monochloroacetate, carried out calorimetrically. Like the earlier investigations in this series [1–5], the present one was performed at 25 °C, in an aqueous medium of unit ionic strength. Sodium perchlorate was used as inert electrolyte.

The stability constants of this system had previously been determined at 20 °C and I = 1.00 *M* with $NaClO_4$ [7]. They have now been re-determined under the experimental conditions adopted here. No determination of the enthalpy and entropy changes of this system has so far been published.

Experimental

The measurements were carried out as described previously and the same notation and procedure of calculation was used [1]. The stock solution of thorium perchlorate was prepared and analyzed as before [7]. The monochloroacetic acid was distilled twice and dried under vacuum. The ligand buffer solutions had to be prepared just before use in order to minimize the hydrolysis of $-CH_2Cl$ group.

The buffer ratio, δ, was equal to 1. Three titrations were performed, with the following initial concentrations of metal ion, C_M^o, and perchloric acid, C_H^o,: 10.00, 7.00; 20.00, 29.43; 30.00, 29.24 m*M*.

For the calculation of the stability constants the least-squares program "Gauss-Z" [8] was used, for the enthalpy changes the least-squares minimizing program "Letagrop Kalle" [9, 10].

Results

From the experimental data (v/ml, E/mV) and the protonation constant of the ligand, $K^H = 4.59 \times 10^2$, determined before [1], the values of $\bar{n}$ and $[L^-]$ were calculated. The complex formation function, $\bar{n}([L^-])$, indicated four mononuclear complexes, whose stability constants values are listed in Table I. The values are in good agreement with those reported before at the same ionic strength and 20 °C [7]. In the same Table, the free energy, enthalpy and entropy changes of the stepwise reactions are also given. The standard deviation in $Q_{corr.}$ was 0.018 cal. The heat of protonation of monochloroacetate had been determined previously [1].

TABLE I. The Stability Constants and the Values of Free Energy, Enthalpy and Entropy Changes for the Stepwise Reactions of the Thorium(IV)–Monochloroacetate System, in 1.00 *M* $NaClO_4$ and 25 °C.

j	β_j (M^{-j})	$-\Delta G_j^o$ (Kcal mol^{-1})	ΔH_j^o (Kcal mol^{-1})	ΔS_j^o (cal mol^{-1} K^{-1})
1	$(5.63 \pm 0.10) \times 10^2$	3.75 ± 0.01	2.92 ± 0.06	22.4 ± 0.2
2	$(4.31 \pm 0.16) \times 10^4$	2.57 ± 0.02	3.11 ± 0.10	19.0 ± 0.3
3	$(6.17 \pm 0.32) \times 10^5$	1.57 ± 0.02	2.56 ± 0.24	13.9 ± 0.9
4	$(3.40 \pm 0.41) \times 10^6$	1.02 ± 0.06	1.91 ± 0.30	9.8 ± 1.1

TABLE II. Comparison of the Thermodynamics of Thorium(IV)–Acetate and –Monochloroacetate Systems, in 1.00 *M* $NaClO_4$ and 25 °C.

		Acetate	Monochloroacetate
$-\Delta G^{o}_{\beta_j}$	j = 1	5.26 ± 0.03	3.75 ± 0.01
	2	9.51 ± 0.03	6.32 ± 0.02
(Kcal mol^{-1})	3	12.20 ± 0.05	7.89 ± 0.03
	4	14.06 ± 0.08	8.91 ± 0.07
	5	15.03 ± 0.10	
$\Delta H^{o}_{\beta_j}$	j = 1	2.70 ± 0.04	2.92 ± 0.06
	2	3.77 ± 0.05	6.03 ± 0.12
(Kcal mol^{-1})	3	7.04 ± 0.10	8.59 ± 0.27
	4	8.28 ± 0.23	10.50 ± 0.40
	5	9.27 ± 0.59	
$\Delta S^{o}_{\beta_j}$	j = 1	26.7 ± 0.2	22.4 ± 0.2
	2	44.5 ± 0.4	41.4 ± 0.5
(cal mol^{-1} K^{-1})	3	64.5 ± 0.8	55.3 ± 1.0
	4	74.9 ± 0.9	65.1 ± 1.6
	5	81.1 ± 2.2	

Discussion

Within the range of $[L^-]$ used here, the fourth mononuclear complex is formed in the present system while the fifth is reached in the acetate system. The stronger complex formation in the latter system is no doubt due to the higher basicity of the ligand, as the interaction between thorium and charged bases is mainly electrostatic [7].

In the monochloroacetate system, the thermodynamic functions do not change abruptly at any step of complexation, both the enthalpy and entropy changes decrease smoothly from the first to the fourth step. No reversal like the one observed in the acetate system takes place. Therefore, if a switch in coordination takes place also with monochloroacetate, it must be at a higher step, not reached in the present measurements. The reason for the difference could be that the acetate ion, by interacting more strongly with the thorium ion, is able to bring about an earlier disruption of the solvate. This seems to be supported by the fact that the overall enthalpy changes, $\Delta H^{o}_{\beta_2}$ for the formation of the complex ThL_2^{2+} are less unfavourable for the acetate than for the monochloroacetate, while the $\Delta S^{o}_{\beta_2}$ terms do not differ very much from each other, Table II.

No switch in coordination has ever been observed in reactions of uranyl(VI) with these carboxylate ligands: the higher charge of thorium ion compared with uranyl(VI), and the circumstance that UO_2^{2+} coordinates only in the equatorial plane, could account for this.

Finally, the values of $\Delta G^{o}_{\beta_4}$, $\Delta H^{o}_{\beta_4}$ and $\Delta S^{o}_{\beta_4}$, *i.e.* the total free energy, enthalpy and entropy changes, of the two systems indicate that the lower stability of the thorium-monochloroacetate complexes as compared with the acetate ones is due both to an ever more unfavourable enthalpy term and to a less favourable entropy term. The lower ligand basicity results in both a weaker metal–ligand interaction and a more extensive hydration of the complexes formed. The smaller $\Delta S^{o}_{\beta_j}$ for monochloroacetate might also be caused by a weaker hydration of the ligand, as compared with acetate.

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