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THERMODYNAMICS OF THE COMPLEX FORMATION OF THORIUM(IV) WITH GLUTATHIONE IN AQUEOUS SOLUTION

ARTURO BISMONDO and LUIGI RIZZO

Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca C.N.R., Corso Stati Uniti 4, 35020 Padova (Italy)

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ABSTRACT

The stability constant for formation of the 1 : 1 thorium(IV)–glutathione complex, and the associated enthalpy and entropy changes were determined by potentiometric and calorimetric titrations. The results are discussed with reference to data obtained earlier with monocarboxylic acid ligands.

INTRODUCTION

A literature survey on the complexation of *f*-block elements with aminoacids or peptides reveals significant disagreement between different authors. We have attempted to clarify the position by studying the interactions between uranyl(VI) and thorium(IV) and some aminoacids [1–3]. As an extension of these studies, we now report the value of the stability constant for the formation of the 1 : 1 thorium(IV) complex with glutathione, together with the corresponding values of enthalpy and entropy changes, determined by potentiometric and calorimetric titrations at 25.0 °C in 1.0 mol dm^{-3} aqueous sodium perchlorate solution.

EXPERIMENTAL

Stock solutions of thorium(IV) perchlorate, containing an excess of perchloric acid, were prepared and standardized as already described [1]. Glutathione (Ega Chemie) was purified from ethanol and dried at 100 °C before weighing. Only freshly prepared solutions were used for titrations, to avoid oxidation of the ligand. Potentiometric measurements were carried out using a Radiometer PHM64-pH meter and calorimetric data were obtained on a Tronac 450 calorimeter. To study the proton–ligand system, solutions containing free glutathione, or glutathione and perchloric acid, were pre-

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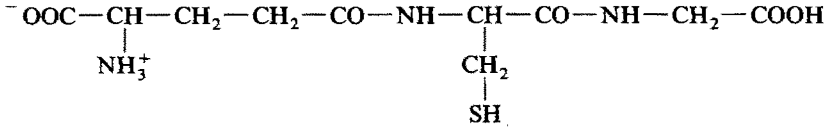
pared and titrated with NaOH solutions. In a typical experiment to investigate the metal–ligand system, a solution of the partially-neutralized ligand was added to an aqueous acid solution of thorium(IV). The values of the formation constants were computed from the potentiometric data using the MINIQUAD program and the values of enthalpies were computed from the calorimetric data using the LETAGROP program. Calculations were performed using a VAX 750 computer. All measurements were carried out under nitrogen at 25.0 °C. The ionic strength of the solutions used was maintained at 1.0 mol dm^{-3}, using sodium perchlorate as neutral salt.

RESULTS AND DISCUSSION

Proton–ligand system

Glutathione is a tripeptide having a glycylcarboxylic acid group at one end and a glutamylcarboxylic acid group at the other. There are also two additional groups, *l*-glutamylammonium and *l*-cysteinyl-sulphydryl, that ionize at pH > 7. At the pH range used in this work (pH < 3), glutathione behaves as a diprotic acid through the two carboxylic acid groups. Therefore we have labelled the ligand HL



$${}^{-}OOC-\underset{NH_3^+}{CH}-CH_2-CH_2-CO-NH-\underset{\underset{SH}{CH_2}}{CH}-CO-NH-CH_2-COOH$$

The equilibrium constant values and the enthalpy changes relative to the protonation were determined for the two carboxylic acid groups only. The values obtained; $\log \beta_1 = 3.50 \pm 0.01\ M^{-1}$ and $\log \beta_2 = 5.78 \pm 0.01\ M^{-1}$, are in fairly good agreement with those ($\log \beta_1 = 3.48\ M^{-1}$ and $\log \beta_2 = 5.56\ M^{-1}$) already reported [4], when account is taken of the different experimental conditions. Our values for the enthalpy changes; $\Delta H_1 = -2.5 \pm 0.3$ kJ mol^{-1} and $\Delta H_2 = -3.8 \pm 0.4$ kJ mol^{-1}, are, however, appreciably different from those reported in ref. 4, viz. $\Delta H_1 = -4.2$ kJ mol^{-1} and $\Delta H_2 = -8.4$ kJ mol^{-1}, which are considered to be of reduced accuracy.

Metal–ligand system

The potentiometric results suggest that only ML_n complexes are formed in aqueous solution. Because of precipitation of insoluble species, the maximum $\bar{n}$ (mean number of coordinated ligands) value obtained was less than 0.8. In a first attempt to interpret the experimental data, the formation of ML and ML_2 species was assumed, but the stability constant of ML_2 proved to be negative and this approach had to be rejected. However, the

TABLE 1

The stability constants and changes in enthalpy and entropy for the formation of thorium(IV) 1 : 1 complexes at 25.0 °C in 1.0 mol dm^{-3} $NaClO_4$ solution (estimated standard deviations in parentheses)

Ligand	log β	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	Ref.
Aminoacetic acid	2.55	4.2	63	1
3-Aminopropanoic acid	3.20	4.2	75	3
4-Aminobutanoic acid	3.44	7.9	92	3
Acetate	3.86	11.3	112	5
Glutathionate	4.27(2)	11.1(6)	119	–

presence in the ligand of two carboxylic acid groups could allow the coordination of two metal ions to one glutathione molecule and hence chain-like polynuclear complexes could be formed. Consequently the possible presence of dinuclear and higher complexes has been tested. The inclusion of these species does not significantly improve the fit, moreover, the degree of formation of polynuclear complexes was very low, except for M_2L. An attempt to calculate values for the thermodynamic functions of M_2L gave a value of log $\beta = 5.30$, corresponding to a value of log $K = 1.03$ for the partial reaction $M + ML = M_2L$ and a degree of formation $< 12\%$. The enthalpy change cannot be determined with sufficient accuracy to allow entropy determination. Moreover, the introduction of the formation constant for this species leads to only very small changes in the value of the corresponding constant for the main species present. In conclusion this species could be present, but only as a minor component. Thus we have considered only ML, the predominant species in the system under investigation and such a model gave a good description of the experimental data, the R factor in the MINIQUAD program being 0.0045. Sufficient heat output could not be achieved in the calorimetric experiments to provide an accurate value for the enthalpy change. The values obtained for the stability constant and enthalpy and entropy changes are reported in Table 1 where the limits of error refer to three standard deviations. For comparison, the complexation data of thorium(IV) with some monocarboxylic acids are also reported. The value of ΔS for the formation of the thorium(IV)–glutathionate complex suggests that the glycylcarboxylate group is bonded to the metal ion. In fact this value of the entropy change ($\Delta S = 119$) indicates that there is, as regards the initial metal charge, an effective lowering of total charge in the complex which contains an anionic ligand (compare the value for the monoacetate complex, $\Delta S = 112$). On the other hand, if the glutamylcarboxylate group coordinates as a neutral group, the complex should have formally the same charge as the free metal ion and the higher charge thus retained should result in a smaller overall entropy gain (compare the values

$\Delta S = 63$, 75, 92 for aminoacetic, 3-aminopropanoic and 4-aminobutanoic acids, respectively).

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