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THORIUM(IV) COMPLEXES OF SOME DICARBOXYLIC ACIDS IN AQUEOUS SOLUTION: A POTENTIOMETRIC AND CALORIMETRIC STUDY

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ABSTRACT

The stability constants and the changes in enthalpy and entropy for the reaction of thorium(IV) ion with ethylene-1,2-dioxydiacetate (edoda) and ethylene-1,2-diaminodiacetate (edda) have been determined in aqueous sodium perchlorate (1.0 mol dm^{-3}) by potentiometric and calorimetric titrations at 25.0 ° C. With the ligand (edoda), formation of 1 : 1 and 1 : 2 chelate complexes has been observed, whereas with (edda), unchelated protonated complexes are present, due to the low pH values at which precipitation of solid compounds occurs. The results are discussed and compared with those of parent uranyl(VI) and samarium(III) complexes.

INTRODUCTION

In the last few years we have studied the thermodynamic properties of aqueous systems containing polydentate ligands and in particular we have reported the changes in the thermodynamic functions ΔG, ΔH and ΔS for the formation of thorium(IV) complexes with the ligands oxydiacetate (oda), iminodiacetate (ida), thiodiacetate (tda) and succinate [1]. The stabilities of the complexes were found to depend on either the chelate ring dimensions or the nature of the donor atom in the carbon chain. The study has been extended to analogous carboxylate ligands containing two donor atoms in the carbon chain, which potentially can form a trichelated moiety. The present paper reports the complexing behaviour of thorium(IV) towards the ligands ethylene-1,2-dioxydiacetate (edoda) and ethylene-1,2-diaminodiacetate (edda) in aqueous solution.

EXPERIMENTAL

Materials

Stock solutions of thorium(IV) perchlorate, sodium hydroxide and sodium perchlorate were obtained and standardized as described elsewhere [2]. The ligand H_2(edoda) was prepared and purified according to the method reported in ref. 3. Commercial H_2(edda) (Ega Chemie) was purified by recrystallization from water. The purity of both ligands was checked by alkalimetric titrations. The ionic strength of all the solutions was maintained at 1.0 mol dm^{-3} using sodium perchlorate as neutral salt.

Procedure

All measurements were carried out under nitrogen at 25.0 °C. Potentiometric measurements were made using our partially automated pH titration unit, consisting of an Apple II personal computer with a real-time clock card, a serial line driver card and a home-made data acquisition and control module based on a Z-80 microprocessor. A Metrohm E-655 digital burette and a Radiometer pH 64 with a glass electrode (Metrohm EA-157) and a double junction Ag/AgCl reference electrode (Metrohm EA-440) were used. The calorimetric measurements to determine the heats of metal complex formation were carried out by using a Tronac model 450 calorimeter. For each system several potentiometric and calorimetric titrations were carried out using starting solutions containing known metal and hydrogen ion concentrations (in the ranges 1×10^{-2} to 3×10^{-2} and 1×10^{-2} to 2×10^{-2}, respectively) titrated with buffer solutions of ligands having different C_{H_2L}/C_{Na_2L} ratios in order to change adequately the concentration of the complexing species and the medium acidity. In a typical experiment a solution of the partially neutralized ligand was added to an aqueous solution of thorium(IV). Calculation of the equilibrium constants from potentiometric measurements was performed using the generalized least-squares program Miniquad. Employing the determined stability constants, the enthalpy changes of the obtained species were calculated from calorimetric titration data by means of the least-squares program Letagrop Kalle. The calculations were performed using a CDC/CRIBER '76 computer.

RESULTS AND DISCUSSION

The thermodynamic functions relative to the formation of (edda) and (edoda) proton complexes have been reported in ref. 4. The formation curves for the thorium(IV)–(edoda) system (Fig. 1) were the result of potentiometric measurements at various metal concentrations and different buffer ratios. The curves superimpose for $\bar{n}$ values in the 0.5–2 interval, whereas their differentiation for $\bar{n} < 0.4$ could be ascribed to mixed complex formation. The curves present a plateau at $n = 2$ and the formation of a 1 : 3 complex was not observed in the range of ligand concentrations reported in Fig. 1. The experimental data were initially treated by assuming the formation of the unprotonated complexes ML and ML_2 along with the protonated

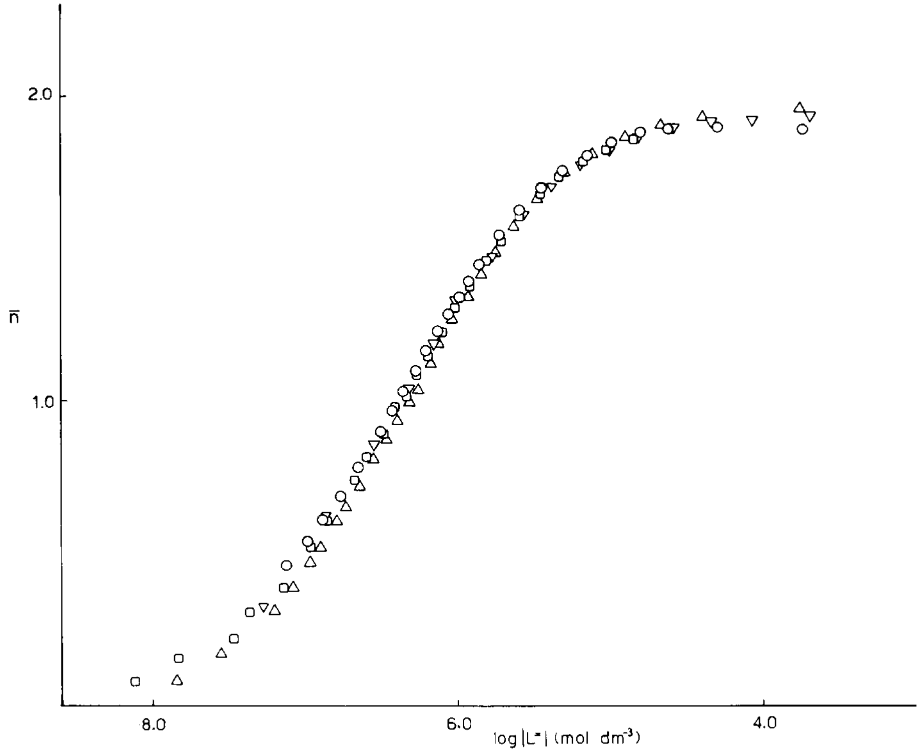

Fig. 1. The complex formation curves of thorium(IV)–(edoda) system. Concentrations in 10^{-3} mol dm^{-3}. ▽ denotes $C_M^{\ominus} = 20.2$, $C_H^{\ominus} = 22.4$ titrated with a $\delta = 2.7$ buffer; ○ and □ and △ denote $C_M^{\ominus} = 10.1$, $C_H^{\ominus} = 11.4$ and $C_M^{\ominus} = 27.9$, $C_H^{\ominus} = 19.1$ and $C_M^{\ominus} = 18.6$, $C_H^{\ominus} = 19.9$, titrated with a $\delta = 0.4$ buffer.

species MHL and MHL_2. Such a model gave, in the Miniquad programm, a good value for the R factor ($R = 0.003$). Moreover the low degree of formation of both protonated species allowed them to be considered as non-significant in the system, the dominating species being ML and ML_2. The potentiometric results have been confirmed by the calorimetric data, the Q_i values (where Q_i is the heat attributable to the formation of the species in the solution) being in accordance with the proposed model. The potentiometric study of the thorium(IV)–(edda) system was limited to a restricted $\bar{n}$ range, owing to the formation of solid products at low pH values. Analogous behaviour was observed for the thorium(IV)–(ida) system, the complexes in solution being ML and MHL [1]. The experimental data of the thorium(IV)–(edda) system were initially treated by a model in which the dominating species were ML, MHL and MH_2L. The results indicated that 2% maximum of the metal was present in solution as ML, whose stability constant was log $\beta = 12.5$. The existence of such a species could not be unequivocally stated, because slight changes in the ligand and proton

TABLE 1

The stability constants and the changes in enthalpy and entropy for the formation of thorium(IV)–(edoda) and –(edda) complexes at 25.0 °C in 1.0 mol dm^{-3} sodium perchlorate medium. The units for the enthalpy and entropy changes are given in kJ mol^{-1} and J mol^{-1} K^{-1}, respectively

Reaction	log β	ΔH	ΔS
Thorium(IV)–(edoda)			
$M+L \rightleftharpoons ML$	6.86 ± 0.03	13.4 ± 0.1	176
$M+2L \rightleftharpoons ML_2$	12.70 ± 0.03	25.4 ± 0.2	328
Thorium(IV)–(edda)			
$M+H+L \rightleftharpoons MHL$	16.23 ± 0.05	-43.6 ± 1.2	165
$M+2H+L \rightleftharpoons MH_2L$	18.78 ± 0.06	-60.2 ± 1.5	158

concentrations yielded negative stability constant values for ML. For this reason the system was treated by a model containing the species MHL and MH_2L, obtaining a fairly good description of the experimental data and a good R factor ($R = 0.0028$). Moreover the model was confirmed by calorimetric data.

The thermodynamic parameters of the systems examined are summarized in Table 1, the quoted errors corresponding to three standard deviations. It is of interest to observe that the stability constant, enthalpy and entropy values for the formation of Th–H_2(edda) (log $K = 2.4$, $\Delta H = 11.5$, $\Delta S = 84$) are very close to those for the formation of the Th–H(ida) complex (log $K = 2.9$, $\Delta H = 7.4$, $\Delta S = 81$) and in accordance with co-ordination of both ligands through one of the carboxylate groups, the closer amino group being protonated. In Table 2 the available data for thorium(IV) complexes with various carboxylates are correlated with those of complexes of uranyl(VI) and samarium(III), the last one chosen as an example of the lanthanide series. The ΔS values of the thorium(IV) 1 : 1 complexes are quite similar to the corresponding value for the thorium(IV) diacetate complex, suggesting a similar solvation change in the reagents upon complexation. The major entropy effect should depend on the association of the thorium(IV) ion with two carboxylato groups, the contribution due to the interaction with chain nitrogen and oxygen being small. A similar trend is observed for the parent uranyl(VI) and samarium(III) systems. The different log β values in the 1 : 1 complex series depend mainly on the ΔH changes, which can be correlated with the different donor properties of the chain heteroatoms.

As shown in Fig. 2, in which the log β_{ML} values for thorium(IV), uranyl(VI) and samarium(III) complexes are plotted as a function of the ligand ΣpK_a, the 1 : 1 complex stability depends on the overall ligand basicity, on the number of chain donor atoms and their affinity towards the metal ion and on the size of the chelate ring. The stability constants of thorium(IV) 1 : 1 complexes with simple dicarboxylates (namely oxalate,

TABLE 2

The stability constants and the changes in enthalpy and entropy for the formation of thorium(IV), uranyl(VI) and samarium(III) 1 : 1 complexes at 25.0 ° C in 1.0 mol dm^{-3} sodium perchlorate medium. The units for the enthalpy and entropy changes are given in kJ mol^{-1} and J mol^{-1} K^{-1}, respectively

Ligands	ΣpK_a	Thorium(IV)				Uranyl(VI)				Samarium(III)			
		log β	ΔH	ΔS	ref.	log β	ΔH	ΔS	ref.	log β	ΔH	ΔS	ref.
Acetate	4.61	3.86	11.3	112	5	2.46	11.8	87	2	2.03 [b]	6.1	59	10
Diacetate		6.97	15.8	186		4.38	17.9	144		3.29 [b]	12.0	103	10
Oxalate	4.59	8.23	–	–	6	5.99 [a]	–	–	6	5.04 [c]	–	–	
Malonate	7.69	7.47	11.9	183	7	5.42	8.9	133	7	3.67	12.5	112	11
Succinate	9.10	6.44	18.6	186	1	3.85	21.7	146	8	–	–	–	
tda	7.13	5.60	20.5	176	1	2.97	14.8	106	9	2.90	11.4	94	12
oda	6.60	8.15	8.4	184	1	5.11	16.9	154	9	5.53	−4.4	91	13
ida	13.77	9.69	6.5	207	1	8.78	−2.2	161	9	6.46 [c]	−3.7	111	14
edoda	6.77	6.86	13.4	176	This work	3.08	27.7	151	4	5.08	1.6	102	15
edda	20.44	–	–	–	–	11.40	–	–	4	8.25	−12.2	117	15

[a] $T = 20$ ° C. [b] $\mu = 2.0$ M ($NaClO_4$). [c] Eu(III).

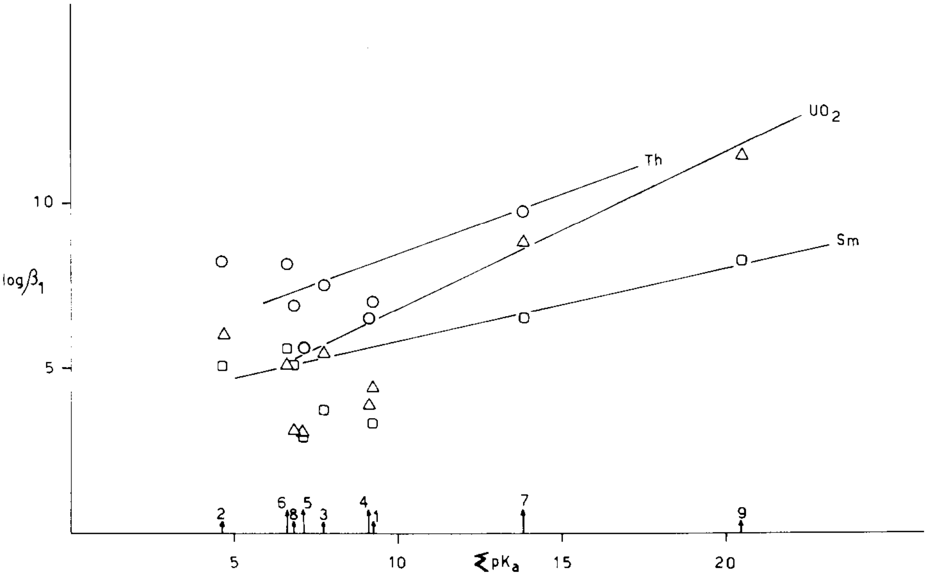

Fig. 2. The variation of log β_1 of 1 : 1 complexation of thorium(IV) (○), uranyl(VI) (△) and samarium(III) (□) as a function of the sum of the pK_a values of the ligands (1, diacetate; 2, oxalate; 3, malonate; 4, succinate; 5, thiodiacetate; 6, oxydiacetate.; 7, iminodiacetate; 8, ethylene-1,2-dioxydiacetate; 9, ethylene-1,2-diaminodiacetate).

malonate and succinate) are in accordance with chelate formation and depend on the chelate ring size. In fact a decrease in stability is observed on going from the five-membered oxalato complex to the seven-membered succinato analogue, in spite of a ligand basicity trend of oxalate < malonate < succinate. Analogous behaviour can be seen in the parent uranyl(VI) and samarium(III) systems. The stability of the iminodiacetate, oxydiacetate and thiodiacetate complexes follows the order (ida) > (oda) > (tda), reversed with respect to basicity of the ligand carboxylato groups [(tda) > (oda) > (ida)] and ascribed to the different donor ability of the chain atoms (NH > 0 > S). Such a trend is confirmed for the potentially tetradentate ligands (edoda) and (edda), the stabilities of the complexes being in the order (edda) > (edoda). The effect of the chain heteroatom on stability depends on their metal affinity. In fact the ligands bearing nitrogen atoms show a stability increasing with the number of chain donors, in the order (edda) > (ida), whereas for the corresponding oxygen donors a reversed trend is observed [(oda > (edoda)].

For the ligands (oda), (edoda), (ida) and (edda) a linear relationship is observed between stability constants of the 1 : 1 complexes and ligand basicities, except for the urany(VI)–(edoda) complex, which is definitely less stable than expected. The uranyl(VI) complexes with the ligands bearing chain oxygen atoms are less stable than the thorium(IV) and samarium(III) analogues, the trend being confirmed in the (oda) series. The lower stability could depend on the electrostatic repulsion among the oxygen atoms crowded around uranium, which could justify the high ΔH values observed for the UO_2-(edoda) and UO_2-(oda) complexes (27.7 and 23.5 kJ mol^{-1}, respectively).

Finally the stability constants of uranyl(VI) and samarium(III) 1 : 1 complexes with simple dicarboxylates and oxydiacetate are of the same order, whereas with the chain nitrogen dicarboxylates an evident stabilization of the uranyl(VI) complexes with respect to the samarium(III) analogues is observed. Such behaviour could suggest a greater affinity of uranyl(VI) for nitrogen than is observed with samarium(III) and, in general, with lanthanide trivalent ions.

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