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Metal-chelate Equilibria of Tl^+, UO_2^{2+}, Th^{4+} with (L)2-amino-butanedioic acid-4-amide in Aqueous Media

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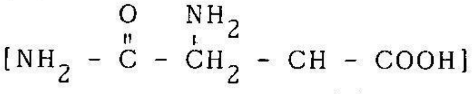
Summary: Interactions between Tl^+, UO_2^{2+}, Th^{4+} and (L)2-amino-butanedioic acid -4-amide have been investigated at different temperatures 25°, 35° and 45°C and ionic strengths μ = [0.0, 0.1, 0.2, 0.5 and 1.0M KNO_3] in aqueous media using a pH titration technique. The data suggest the formation of 1:1 complex with Tl^+ and UO_2^{2+} and 1:1 and 1:2 complexes with Th^{4+} ions in the pH range 6.3-9.2, 3.3-6.0 and 2.5-5.5 respectively. Formation constants have been evaluated employing Calvin and Melchior's extension of Bjerrum's method. The thermodynamic stability constants and other functions $-\Delta G°$, $\Delta H°$ and $\Delta S°$ accompanying complexation have also been evaluated.

Introduction

The study of metal-amino acid complexes is of great importance from biological point of view as it contributes to a better understanding of metal protein interactions. In a comprehensive programme, Saxena and coworkers [1-4] have carried out extensive studies on the electrochemical behaviour of amino acids and their complexation with several metal ions which have found useful applications in biochemistry and medicine [5].

The present communication, which is part of a programme describes potentiometric investigations on the Tl^+, UO_2^{2+} and Th^{4+} complexes with (L)2-aminobutanedioicacid-4-amide



$$[NH_2 - \overset{\overset{\displaystyle O}{\parallel}}{C} - CH_2 - \overset{\overset{\displaystyle NH_2}{|}}{CH} - COOH]$$

their composition, stability constants and thermodynamic functions at different temperatures and ionic strengths employing Calvin and Melchior's extention [6] of Bjerrum's [7] pH titration technique.

Experimental

(L)2-Aminobutanedioic acid-4-amide [referred herein as H_2A] was supplied by B.D.H. Chemicals Ltd. Poole, England. Metal nitrates [$TlNO_3$ $UO_2(NO_3)_2 6H_2O$, $Th(NO_3)_4 6H_2O$] and other reagents used were also of Analar R.B.D.H. quality.

Procedure

pH measurements were made on a Toshniwal digital pH meter with glass calomel electrode assembly (accuracy ± 0.01pH). The temperature of the cell was maintained by a thermostat having an accuracy of ± 0.1°C. Requisite amounts of KNO_3 were added to the solution mixture for maintaining ionic strengths.

The experimental procedure as described earlier [4] involves a series of pH titration of the ligand with standard NaOH in the absence and presence of metal ions at different metal-ligand ratio.

The stability constants of metal-ligand complexes at different temperatures 25°, 35° and 45°C and ionic strengths 0.1, 0.2, 0.5 and 1.0M were evaluated by employing Calvin and Melchior's extension of Bjerrum's pH titration technique keeping the ratio of metal to ligand constant at 1:5, using 4 x 10^{-3}M $HClO_4$ for initial lowering of buffer region.

The stoichiometry of complex formed in solution was determined by the titration of ligand solution alone and with varying amounts of metal in metal :ligand ratio of 1:1, 1:2 and 1:4 done in 0.1M NaOH. Curves were plotted between pH and moles of alkali required per mole of ligand 'm' (Fig.1) and from the inflections in the curves, metal-ligand combining ratio was obtained. The nature of chelation equilibria has been explained and the equilibrium constants are evaluated using standard procedures [8,9].

Results and discussion

From the curves in Fig.1, it is evident that the addition of equimolar concentration of metal ion results in the lowering of buffer region and decrease in the pH of the solution due to proton displacement indicating the complex formation. The pH effect has been used as quantitative measure of stability of metal chelates [8]. The pH drop for the ions of Th^{4+} and UO_2^{2+} is much larger than for Tl^+ with respect to ligand (curve a,b,c and d). This observation shows that Th^{4+} and UO_2^{2+} ions have greater tendency to form chelates as compared to Tl^+ and their relative stabilities. This has been borne out by the higher stability constants of UO_2^{2+} and Th^{4+} complexes in comparison to those of Tl^+ [Table 1].

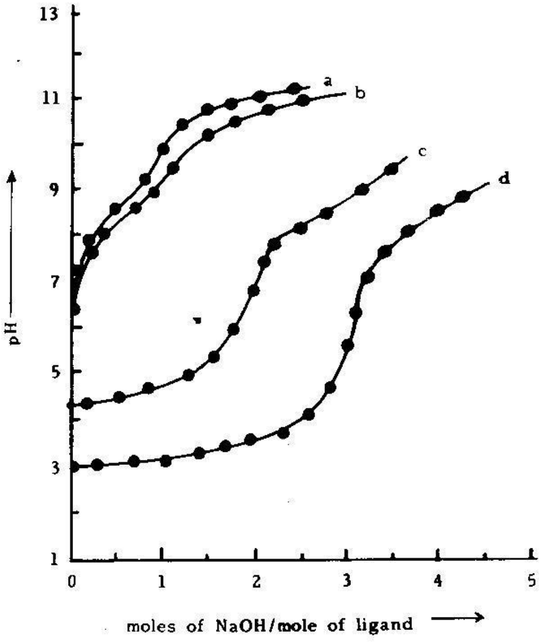


Fig.1: pH metric titration of the solutions.

Curve(a) $4x10^{-3}M\ H_2A$

(b) $4x10^{-3}M\ H_2A+4x10^{-3}MH^-$

(c) $4x10^{-3}M\ H_2A+4x10^{-3}M\ VO_2^+$

(d) $4x10^{-3}M\ H_2A+4x10^{-3}MTh^{4+}$

In the case of Tl^+, the inflection of m = 1 suggests the formation of 1:1 complex in the pH range 6.3-9.2 beyond which precipitation occurs. Since the ligand species in the pH range is the monovalent anion, HA^-, the interaction with Tl^+ ions is as follows:

$$Tl^+ + HA^- \rightleftharpoons TlA^- + H^+;\quad H^+ + OH^- \longrightarrow H_2O$$

$$K = \frac{[TlA^-]}{[Tl^+][HA^-]}$$

Table-1: Metal-ligand stability constants and thermodynamic functions of complexes of Tl^+, UO_2^{2+}, Th^{4+} with (L)2-amino butanedioicacid-4-amide

Metal complex species	t°=25° μ=0.1	log K stability constants 35°					45°	Thermodynamic functions t°C = 35		
		0.0	0.1	0.2	0.5	1.0	0.1M	Δ G° (Kcal/mole)	Δ H° (Kcal/mole)	Δ S° (cal/deg/mole)
TlA^-	3.40	3.55	3.60	3.65	3.78	3.90	3.85	-5.0	9.8	48.2
log β	3.40	3.55	3.60	3.65	3.78	3.90	3.85			
$[UO_2HA^+]$	7.25	7.35	7.40	7.45	7.60	7.80	7.55			
$[UO_2A]$	6.35	6.45	6.50	6.55	6.72	6.85	6.65	-19.6	13.0	105.8
log β calculated	13.60	13.80	13.90	14.00	14.32	14.65	14.20			
Exptl.		13.85								
$[ThHA^{3+}]$	8.35	8.45	8.50	8.55	8.72	8.90	8.65			
$[ThA^{2+}]$	7.65	7.75	7.80	7.85	8.00	8.25	8.00	-33.5	22.9	183.4
$[ThA_2]$	7.40	7.45	7.50	7.55	7.69	7.80	7.80			
log β calculated	23.40	23.65	23.80	23.95	23.41	24.95	24.45			
Exptl.		23.75								

In case of UO_2^{2+}, there is significant lowering of buffer region and the inflection at m = 2 suggests the formation of 1:1 overlapping [protonated and unprotonated] complexes in the pH range 3.3-6.0 beyond which precipitation occurs.

$$UO_2^{2+} + H_2A \rightleftharpoons [UO_2HA^+] + H^+;$$

$$H^+ + OH^- \rightarrow H_2O$$

$$K = \frac{[UO_2HA^+]}{[UO_2^{2+}][H_2A]}$$

$$UO_2HA^+ \rightleftharpoons UO_2A + H^+ ;$$

$$H^+ + OH^- \rightarrow H_2O$$

$$K = \frac{[UO_2A]}{[UO_2HA^+]}$$

Similarly with Th^{4+}, the buffer region is lowered to a considerable extent and inflection at m = 3 suggests the formation of 1:1 (protonated and unprotonated) complexes which would result in the disproportionation forming 1:2 overlapping complex in the pH range 2.5-5.5 beyond which precipitation occurs.

$$Th^{4+} + H_2A \rightleftharpoons ThHA^{3+} + H^+ ;$$

$$H^+ + OH^- \rightarrow H_2O$$

$$K = \frac{[ThHA^{3+}]}{[Th^{4+}][H_2A]}$$

$$ThHA^{3+} \rightleftharpoons ThA^{2+} + H^+ ;$$

$$H^+ + OH^- \rightarrow H_2O$$

$$K = \frac{[ThA^{2+}]}{[ThHA^{3+}]}$$

In the above equilibria, H^+ ions liberated are removed from the system forming H_2O molecule, whose concentration remains practically constant during the course of reaction and hence it is not taken into consideration in the calculation of equilibrium constants

$$ThA^{2+} + OH^- \rightleftharpoons \tfrac{1}{2}ThA_2 + \tfrac{1}{2}Th(OH)_2^{2+}$$

$$K = \frac{[ThA_2]^{\frac{1}{2}}}{[ThA^{2+}]} \quad \text{(ignoring the concentration of other species)}$$

The titrations were repeated with 1:2 and 1:4 (metal:ligand) ratios which also confirm the above results and there was no indication of polynuclear complex formation.

Stability constants

In order to determine the stability constants of various species formed in solution, the values of formation function n and free ligand exponent (pA) were calculated by Bjerrum's method using the values of dissociation constants of the ligand at different temperatures and ionic strengths already reported by the authors [10]. Formation constants were evaluated at n = 0.5, 1.5 and 2.5. These stability constants are presented in Table 1 and follow the order

$$Th^{4+} > UO_2^{2+} > Tl^+$$

The higher stability of Th^{4+} complexes relative to those of UO_2^{2+} and Tl^+ is due to high positive charge. The stability constants increase with temperature which shows that higher temperature is favourable for the formation of complexes and for their stabilities. These values are also found to increase with increase in ionic strengths and linear plots were observed when log K values were plotted against ionic strengths (μ). Thermodynamic stability constants were obtained by extrapolating the experimentally determined stability constants to zero ionic strengths.

Thermodynamic parameters

The values of free energy (Δ G°), enthalpy (Δ H°) and entropy (Δ S°) accompanying complexation have been determined at 35°C with the help of standard equations [11] and are summarized in Table 1.

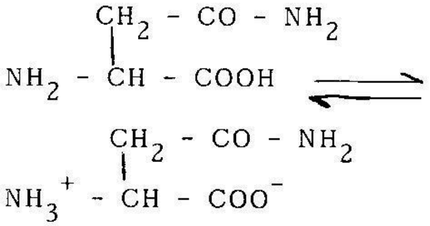
The negative value of Δ G° shows that the reaction tends to proceed spontaneously. The positive value of enthalpy shows endothermic nature of the reaction suggesting that higher temperature favours chelation process, in fair agreement with increasing stability with temperature. The positive values of entropy also favour the chelation process.

Metal-chelate structure

In order to elucidate the structure of metal chelates formed in solution, the following factors have been considered:

1. The coordination site of the donor group available in the ligand and the basicity.
2. The coordination number of metal ion.
3. The composition of highest stable species of chelate formed in solution by the interaction of metal ions with chelating agents.

In the present work, the title ligand has two strong donor groups, one is the nitrogen of amino group and second is oxygen of carboxyl group. However, amide group present in ligand has weak coordinating tendency and as such metal coordinates through the nitrogen of the amino group and oxygen of the carboxyl group. The generally accepted structure of asparagine in aqueous solution is one in which the carboxylic acid group is one has interacted with the amino nitrogen to form a dipolar ion



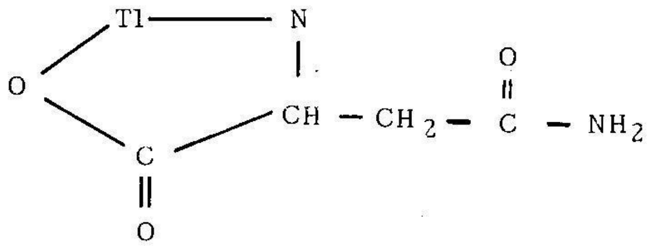
$$NH_2-\overset{\overset{\displaystyle CH_2-CO-NH_2}{|}}{CH}-COOH \rightleftharpoons NH_3^+-\overset{\overset{\displaystyle CH_2-CO-NH_2}{|}}{CH}-COO^-$$

Metal ions exist in solution as aquo complexes, and their properties are influenced to a considerable extent by the nature and oxidation state of the central metal atom. The formation of metal complexes of amino acids containing one amino and one carboxyl group takes place by involving the binding of the anion of the amino acid by the metal ion.

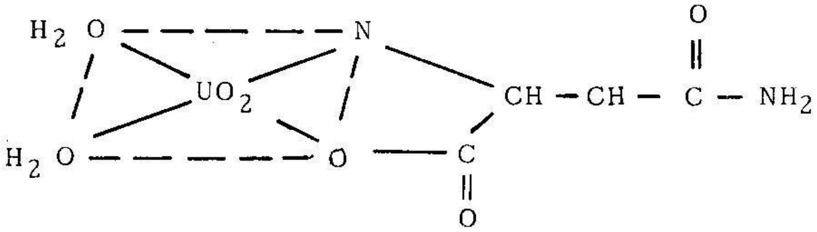
The metal ions involved in the chelate formation have coordination number 2, 4 and 6 for Tl^+, UO_2^{2+} and Th^{4+} respectively [8]. As such the cyclic structure for Tl^+, octahedral structure for UO_2^{2+} (oxo ion) which seems to have coordination requirement of four donor groups in addition to the bound oxygen atoms, and octahedral structure for Th^{4+} having coordination requirement six have been suggested. The arrangement for Th^{4+} of coordination requirement eight is doubtful [8].

Taking into consideration, the above factors along with the stable species of the metal-chelates formed, as is evident from the stoichiometric consideration, the following probable structures are suggested.

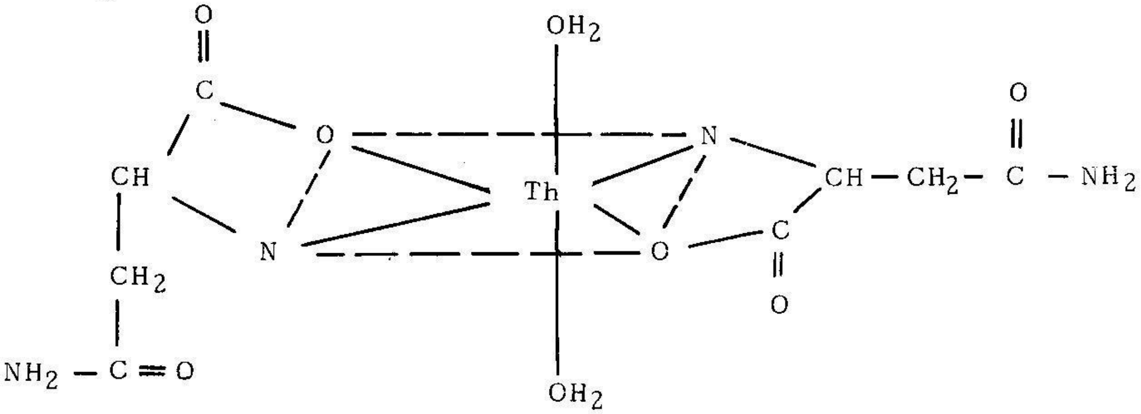
i) TlA^-



ii) UO_2A



iii) ThA_2



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