Study and Calculation of Stability Constants of Molybdenum (VI) Complex with Cytosine

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Abstract

Formation equilibria of molybdate ion (MoO_4^{2-}) complex with cytosine in pH=5.8 has been investigated by spectrophotometric measurements in aqueous solution at 0.15 mol lit^{-1} ionic strength ($NaClO_4$), and $25 \pm 0.1°C$. In this condition the 1:1 complex has the formula MoO_4L^{2-}, where L represents the base of DNA. The stability constants of the complexes formed and their stoichiometries are given and interpreted. The logarithms of the cumulative stability constant β_{xyz} of the complex: $[(H)_x(oxometal)_y(cytosine)_z]$, is log $\beta_{211} = 17.321$.

Keywords: Molybdenum(VI), Cytosine, Stability constant

Introduction

Molybdenum as a trace element plays an important role in metabolic processes[21] Complexes of molybdenum(V) and molybdenum(VI) with base of DNA and organic sulphur compounds[22] are of interest as models for molybdenum-containing enzymes. These enzymes are known to catalyse a number of important biological oxo- transfer reactions where the valence of molybdenum alternates between molybdenum(VI) and molybdenum(IV) states in reactions with substrates and subsequent reactivation [23] There have been many studies of the complex of molybdenum (VI) with α-amino acids[4-7] and some amino polycarboxylicacids (NTA, EDTA, MIDA, IDA)[4,8-14], but to our knowledge,there is no report about the formation of complex of Mo (VI) with cytosine. This metal- ligand equilibrium was studied at 25°C with 0.15 mol lit^{-1} sodium perchlorate as ionic medium. These thermodynamic results allow us to speculate on the structure of the complex obtained.

EXPERIMENTAL

Reagents- Sodium perchlorate, Sodium molybdate, Perchloric acid, Sodium hydroxide

and cytosine were obtained from E. Merck as analytical reagent grade materials and were used without any purification. Dilute perchloric acid solutions were standardized against K(HCO3).

A 50% Sodium hydroxide solution free from carbonate was prepared from the commercial. p.a.material filtered through a G4 jena Glass filter and stored in a polyethylene bottle; dilute solutions were prepared from boiled distilled water and this stock solution and were standardized titrimetrically against a standard iron (II) sulphate solution.15 All dilute solutions were prepared from double- distilled water, with specific conductance equal to $(1.3 \pm 0.1)\ \mu\Omega^{-1}cm^{-1}$.

Measurements- All measurements were carried out at 25 ± 0.1°C, the ionic strength was maintained at 0.15 mol lit^{-1} with sodium perchlorate. A Horiba D-14 pH-meter was used for pH measurements. The pH meter has a sensitivity of 0.01 units. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. The calibration has been done for the whole pH(pH = -log[H+]) range used. Spectrophotometric measurements were performed on a UV-vis Shimadzu 2101 spectrophotometer with an Acer Mate 486 SX/250 computer using thermostated, matched 10-mm quartz cells. The measurement cell was of the flow type. A Masterflux pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so that the absorbance and pH of the solution could be measured simultaneously.

RESULTS AND DISCUSSION

The protonation constants of cytosine have been extensively studied in protonation constants of background electrolytes, and the results are reported in the literature. The following equilibria were studied, where L^- represents the fully dissociated cytosine anion: $H^+ + L^- \Leftrightarrow HL \qquad K_1 = [HL]/[H^+][L^-]$ (1

$H^+ + HL \Leftrightarrow H_2L^+ \quad K_2 = [H_2L^+]/[H^+][HL] \quad (2$

The protonation constants of the imido, k_1, and the second imino groups, K_2, of the side chain of the cytosine, base of DNA, has been determined using potentiometric techniques that shown in Figure 1, calculated using a computer program(Excel) that employs a least- squares method[16].

The protonation constants, expressed as log K, are collected in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.

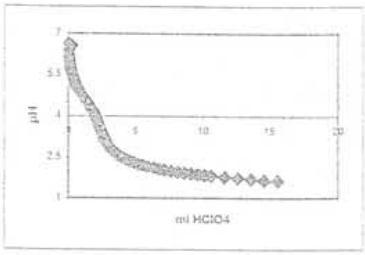

Figure 1: Plot of pH of cytosine, vs the millilitres of $HClO_4$ 0.1 mol lit^{-1} at 0.15 mol lit^{-1} ionic Strengths of $NaClO_4$, 25±0.1°C ,and 50 ml of ligand of cytosine 0.005 mol lit^{-1}.

Table 1. Protonation constants of the imido, K_1, and the second imino groups, K_2, of cytosine at 0.15 mol lit^{-1} ionic strengths of $NaClO_4$.

log K_2	log K_1	Experimental conditions	Ref
3.93 ± 0.05	11.85 ± 0.04	I=0.15M, $NaClO_4$, t= 25°C	This work
4.40	12.50		[20]

Spectrophotometric results

The absorbances of the solution of Mo(VI) and cytosine at a total concentration of 10^{-4} mol dm^{-3} in the UV range (255 to 270 nm) at a constant pH of 5.8 [5,25,26] were determined.

The variation of absorbance of Mo[VI] and complex versus plot shown in Figure 1. It shows that the appropriate range of plot for complex formation is 5.5 to 6.5.

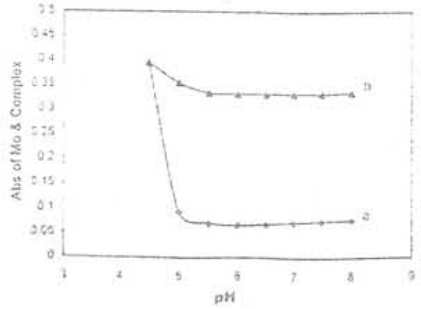

Figure 2:

a) Plots of the absorbance of MoO_3L^{2-}, Abs. vs pH. At [Mo(VI)-cyto]= 3×10^{-3} M at 25±0.1°C , Ionic strengths of 0.15 m $NaClO_4$, and λ =270nm

b) Continuous variation plot of the absorbance of complex, Abs. vs pH at [Cyto]= $5\times10^{-5}M$, [Mo(VI)]= 5×10^{-5} M, at 25±0.1°C , ionic strengths of 0.15M $NaClO_4$ and λ = 260nm

The observed absorbances were corrected from eq 3-13:

$$A_c = A_{obs} - \varepsilon_M(C_M - [C]) - \varepsilon_L(C_L - [C]) \quad (3)$$

In the little concentration of Mo, $C_M \approx [C]$:

$$A_c = A_{obs} - \varepsilon_L(C_L - C_M) \quad (4)$$

$$A_{obs} - \varepsilon_L[L] = A_c \quad (5)$$

$$A_c = \varepsilon_C[C] \quad (6)$$

$$A_c = A_{obs} - \varepsilon_M(C_M - [C]) - \varepsilon_L(C_L - [C]) = \varepsilon_c[C] \quad (7)$$

$$[C] = \frac{A_{obs} - \varepsilon_M C_M - \varepsilon_L C_L}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (8)$$

$$[M] = C_M - [C] = C_M - = \frac{A_{obs} - \varepsilon_M C_M - \varepsilon_L C_L}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (9)$$

$$[M] = \frac{\varepsilon_C C_M - A_{obs}}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (10)$$

$$[L] = C_L - [C] = C_L - \frac{A_{obs} - \varepsilon_M C_M - \varepsilon_L C_L}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (11)$$

$$[L] = \frac{\varepsilon_C C_L - \varepsilon_M C_L - A_{obs} + \varepsilon_M C_M}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (12)$$

$$A_C = \frac{\varepsilon_C A_{obs} - \varepsilon_M \varepsilon_C C_M - \varepsilon_L \varepsilon_C \varepsilon_L - \varepsilon_L \varepsilon_M C_M + \varepsilon_L \varepsilon_M \varepsilon_L}{\varepsilon_C - \varepsilon_M - \varepsilon_L} \quad (13)$$

For the determination of molar Absorptivities coefficient of Mo(VI) have been prepared its solutions with different concentertion, and have been measured their absorbance . the results shown in Table 2 and Figure 3.

Table2. Absorbance values the soloution of Molybdenum (VI) at different Concentration and Wavelengths pH= 5.8 at 25 ± 0.1 °c and ionice strength of 0.15M $NaClO_4$

C_M	Abs			
	255- λ	260- λ	265- λ	270- λ
0.012	0.6008	0.3064	0.1528	0.0696
0.0004	0.188	0.104	0.0536	0.0264
0.0001	0.0456	0.024	0.0112	0.056

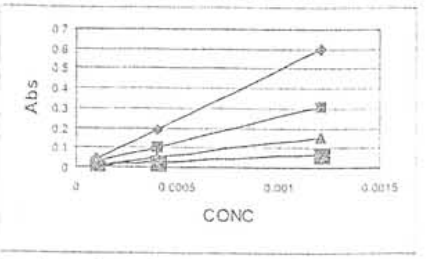

Figure3. Continuous Variation plots of the absorbance of Soloutions of Molybdenum (VI) at different Concentration at λ = 255, 260 , 265 and 270 nm , pH= 5.8 at 25 ± 0.1 °c and ionic strength of 0.15 M $NaClO_4$

Table 3. Molar Absorptivities of Mo (VI), ε_M , Cyto, ε_L , and MoO_3L^{2-}, ε_c , at pH=5.8, 25 ± 0.1 °C , different wavelengths, [Mo(VI)+Cyto]=10^{-4}M, and ionic strength of 0.15M $NaClO_4$

λ(nm)	255	260	265	270
ε_M	450	240	112	56
ε_L	5304	6048	6392	6032
ε_C	6128	6736	6864	6224

By the known of values of the total Concentration of metal and ligand , also values of ε_M , ε_L , ε_C and Absorbance were observed, we can calculateThe absorbance were corrected values of the Absorbance were corrected at defferent wavelengths,and different mole Fraction of metal ,shown in teble 4.

Table4. The absorbance Were corrected of Complex at pH = 5.8 and experimental conditions in each the soloution of job [Mo(VI) – Cyto] = 10^{-4} M

$\frac{X_M}{X_M + X_L}$	A_C			
	255-λ	260-λ	265-λ	270-λ
0.1	0.06128	0.0581	0.0521	0.06224
0.2	0.11	0.092	0.07353	0.18
0.4	0.2167	0.187	0.168	0.447
0.5	0.2936	0.274	0.268	0.58
0.6	0.195	0.1743	0.132	0.368
0.8	0.082	0.066	0.041	0.132
0.9	0.0324	0.021	0.01632	0.053

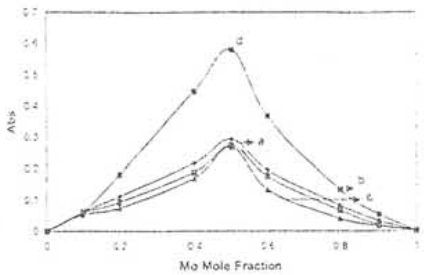

Figure 4. Continuous variation plots of the absorbance of MoO_3L^{2-}, Abs. vs the mole fraction of Mo(VI), at 25 ± 0.1 °C , pH=5.8, ionic strength of 0.15M $NaClO_4$, and [M]+[L]=10^{-4}M.

A_c, A_{obs}, and ε_M are the absorbance of the complex and the observed absorbance and the molar absorptivity of Mo, respectively. ε_M values were calculated at a mole fraction of Mo equal to 2 and are shown in Table 1. In figure 3, a maximum at a mole fraction of Mo equal to 0.5 was obtained, indicating a 1:1 complex.

The complex $H_xM_y(cytos)_z^{(x+ny-z)+}$ formed is characterized by its stoichiometry (x:y:z). The stability constant of the complexation equilibrium (14) is defined by β_{xyz} (15):

$$xH^+ + yM^{n+} + zCytos^- \Leftrightarrow H_xM_y(Cytos)_z^{(x+ny-z)+} \quad (14)$$

$$\text{with} \quad \beta_{xyz} = \frac{[H_xM_y(Cytos)_z^{(x+ny-z)+}]}{[H^+]^x[M^{n+}]^y[Cytos^-]^z} \quad (15)$$

In aqueous solution cytosine exists in its anionic from ($cytos^-$). Zwitterionic species (Hcytos) and cationic from (H_2cytos^+).

The protonation constants of cytosine have been used for computation of the stability constants have been found in the literature.[17]
Result of computation is given in table 5:

Table 5. Metal complexes formation constants for cytosine in 0.15 M $NaClO_4$ at 25°C (x,y and z are the stoichiometric coefficients of the complex who correspond respectively to the proton, metal and ligand)

Complex	Stiochiometry of complex (x:y:z)	log β_{xyz}	Ref
Mo(VI) + Cytosine	2:1:1	17.321 ± 0.015	this work

Our complexation studies of molybdenum (VI) ion with cytosine shows only the formation of $MoO_3(cytos)^{2-}$ complex species.

For the more consider and comparative, see the table 6. The structure of sodium molybdate is believed to be octahedral in solution [24] with three positions to form its complexes with a tridentate ligand like cysteine or histidine and aspartic acid. These complexes usually have great stability constants to confirm this speculation (table 6). Values of log β obtained for Mo(VI) + histidine, cysteine and aspartic acid systems (table 6) are greater than that of the Mo(VI) + cytosine in the order of their stability constants: cytosine< aspartic acid < histidine < cysteine.

Assuming that these amino acids are all tridentate ligands in their molybdenum (VI) complexes [5,25-26] , but cytosine is potentially a bidentate ligand toward metal ions.On the other hand, Mo(VI) will bond with this bidentate ligand, with two donor sites.

Thus, this is that same acts that we expected.

Table 6. Averege values of logβ at various wavelengths at pH=5.8

logβ	experimental conditions	ref
21.4±0.1	cysteine+ Mo(VI) I=0.1 M NaClO , 25°c	5
18.37	histidine+ Mo(VI) I=0.1 M NaClO , 25°c	25
18.2	aspartic acid+ Mo(VI) I=0.15M NaClO , 25°c	26
17.321±0.01	cytosine+ Mo(VI) I=0.15M NaClO , 25°c	this work

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