COMPOSITION AND STABILITY OF THE COMPLEXES OF TRANSITION METAL IONS WITH OXINE AND VITAMIN U

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ABSTRACT

The formation of ternary complexes of transition metal ions with oxine as primary ligand (A) and vitamin U as secondary ligand (L) has been carried out pH metrically at $25 \pm 0.1^\circ$C and $35 \pm 0.1^\circ$C. The ionic strength was maintained at $\mu = 0.2$ M dm^{-3}. The log K values for these complexes were determined at 25°C and 35°C. The values of ΔG, ΔH and ΔS for complexation at 35°C are reported.

Key Words: Stability constants, Potentiometric studies, Transition metal ions, Ternary complexes.

INTRODUCTION

Amino acids have wide applications in the fields of biochemistry and pharmaceutical industries[1]. Ternary complexes involving biomolecules serve as useful model for *in vivo* enzyme–metal ions complexes involved in metallo–enzyme catalysed biological reactions[2,3]. Amino acid containing active – NH$_2$ and –COOH groups have a wide variety of applications in medicine, biology, chemical and other fields. Several metal ions have the ability of complex formation with amino acids, which are involved in several metabolic and enzymatic activities of human beings and have a key role in nitrogen assimilation. Saxena et al.[4–6] have studied several such metal complexes of amino acids, which have found useful applications in biological and pharmaceutical fields.

The present communication describes the chemistry of transition metal ion complexes with oxine and vitamin U; their composition, stability constant and thermodynamic functions and accompanying the complexation reactions at different temperatures. There is no reference in the literature on such investigations and hence, this work has been under taken.

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EXPERIMENTAL

Oxine, vitamin U sodium perchlorate (all Fluka), perchloric acid (BDH) and sodium hydroxide (Analar R) were used.

Stock solutions of $Cr(ClO_4)_3$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$ and $Cu(ClO_4)_2$ were prepared and standardized with EDTA solution[7]. Carbonate free sodium hydroxide solution was used for carrying out titrations. Digital μ pH–meter 361 with readability ± 0.01 was used for pH–metric measurements. Modified form of Irving – Rossotti titration technique has been used[8,9]. The 1 : 1 : 1 molar ratio of M, A and L was maintained in the solution. The ionic strength of the solution was maintained at 0.2 M dm^{-3} using $NaClO_4$. Five sets of the solution were prepared containing:

(i)   Known amount of $HClO_4$,

(ii) Free $HClO_4$ + known amount of primary ligand,

(iii) Free $HClO_4$ + known amount of secondary ligand,

(iv) Free $HClO_4$ + known amount of primary ligand + known amount of metal perchlorate, and

(v) Free $HClO_4$ + known amount of primary ligand + known amount of secondary ligand + known amount of metalperchlorate

Total volume of each mixture was raised to 50 mL using double distilled water. From titration data given in Fig. 1, $\bar{n}H$, $\bar{n}$ and pL were calculated using Excel computer programme on the basis of literature[10, 11].
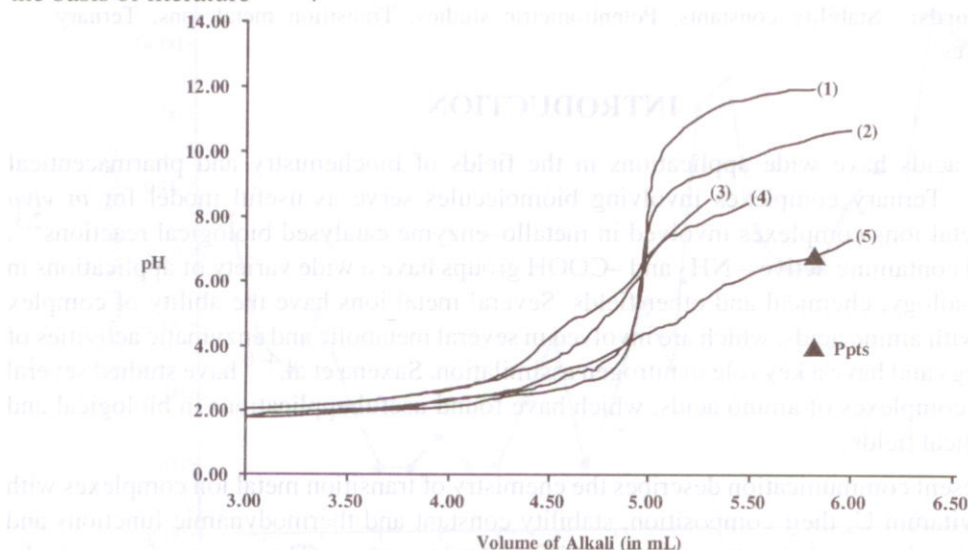

Fig. 1. Cu (II)–Oxine– Vitamin U system temperature 25 ± 0.1°C. (i) Acid, (ii) Oxine, (iii) Vitamin U, (iv) 1 : 1 molar ratio of Cu (II)–Oxine, (v) 1 : 1 : 1 molar ratio of Cu (II)–Oxine–Vitamin U

Stability Constants

The values of proton ligand stability and metal ligand stability constants for transition metal ion complexes with oxine and vitamin U at 25°C and 35°C are given in Table 1.

Table 1. Proton ligand and metal ligand stability constants of transition metal complexes of oxine and vitamin U at different temperature ($\mu = 0.2$ M NaClO$_4$)

Temp.	Ligand vitamin U	Metal – Ligand Stability Constants			
		$\log K_{Cr.AL}^{Cr.A}$	$\log K_{Co.AL}^{Co.A}$	$\log K_{Ni.AL}^{Ni.A}$	$\log K_{Cu.AL}^{Cu.A}$
25°C	$pK_1^H = 8.25$	6.05	6.15	6.25	6.35
	$pK_2^H = 2.17$				
35°C	$pK_1^H = 8.15$	6.16	6.25	6.32	6.46
	$pK_2^H = 2.02$				

Where A = oxine; L = vitamin U

Thermodynamic Functions

The overall changes in thermodynamic functions, free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reaction have been determined at 35°C with the help of following equation and are given in Table 2.

$\Delta G = -$ RT in β, where β is the overall stability constants of the complexes.

(ΔH) is determined with the help of the following equation.

$$\frac{d \ln \beta}{dT} = \frac{\Delta H}{RT^2}$$

ΔS was evaluated from the relation, $\Delta S = \dfrac{\Delta H - \Delta G}{T}$

Table 2. Thermodynamic functions of transition metal complexes with oxine and vitamin U

Metal Complexes	Temperature 35°C		
	ΔG Kcal mole^{-1}	ΔH Kcal mole^{-1}	ΔS Kcal mole^{-1} deg^{-1}.
Cr. A.L.	-8.68	4.62	0.0432
Co. A.L.	-8.81	4.20	0.0422
Ni. A.L.	-8.91	2.94	0.0385
Cu. A.L.	-8.10	4.62	0.0446

where A = oxine; L = vitamin U

RESULTS AND DISCUSSION

The formation of ternary complex can be represented as follows:

$$[MA] + HL \xrightleftharpoons{-H^+} [MAL]$$

$$K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]}$$
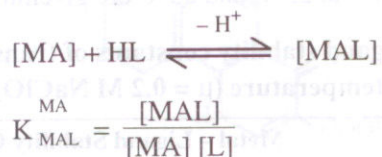
Where,

M	=	Cr (III), Co (II), Ni (II) and Cu (II)
HA	=	Oxine
HL	=	Vitamin U, and
MA	=	Complex of metal with oxine

The mixed ligand stability constants of 1 : 1 : 1 ternary complexesof [M (III)–oxine–vitamin U] and [M (II)–oxine–vitamin U] were calculated, considering that 1 : 1 [M (III) oxine]$^{2+}$ and [M (II)oxine]$^+$ are completely formed before coordination of secondary ligand takes place. The formation of [M (III)–oxine–vitamin U] and [M (II)–oxine–vitamin U] are expected to take place by following mechanism.

$$[M (III).A.2H_2O]^{2+} + L^-$$

$$\downarrow$$

$$[M(III).A.H_2O]^{2+}.H_2O$$

$$\downarrow$$

$$[M(III).A.L]^+ + H_2O$$
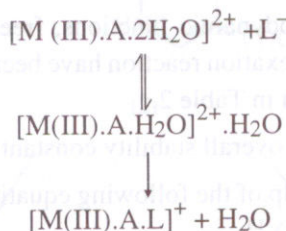
(Like wise the divalent metal ions give [M(II).A.L]

$\bar{n}$ and pL values for 1 : 1 complex system were calculated using the equations given by Irving Rossotti[12]. More precise values of log K_{MAL}^{MA} were calculated by method of linear plot[13].

The mixed ligand formation constant value of Cr–oxine–vitamin U is lower than those of Co, Ni and Cu divalent ions. The presence of –COOH groups on two chelating nitrogen atoms has lowered the value of formation constants of mixed ligand complexes.

The [Cu–oxine–vitamin U] complex has higher value of formation constant than corresponding Cr (III), Co (II) and Ni (II) complexes. Some of first representatives of transition series elements show simple chemical behaviour in their complexes. The properties and behaviour can be explained as follows:

(i) Ionization enthalpies of metal atoms (ii) Ionic radius (iii) Electronic structure of metal ions (iv) Nature of the concerned ligands: mainly $d\pi$–$p\pi$ interactions and (v) Stereochemistry of the complex or crystal structure.

Chromium shows stable tri and hexa oxidation states, and the trivalent chromium was selected for this work. The stability constant of chromium–oxine–vitamin U complex is lower than that of Co (II), Ni (II) and Cu (II). (Cr^{3+} : log K_{MAL}^{MA} = 6.05 at 25°C and 6.16 at 35°C).

Co, Ni and Cu all bivalent ions were selected for equilibrium study for chelation with the primary ligand oxine with the secondary ligand vitamin U, which coordinates through N and O of $-NH_2$ and $-COOH$ groups, respectively. Cobalt is a ferromagnetic metal with low value of Co^{2+}/Co potential (– 0.277 v); however, it is not highly reactive. Nickel has a stable +2 oxidation state. Its higher oxidation states are comparatively unstable. Nickel is also ferromagnetic. Nickel ions have coordination numbers (6, 5 and 4). This ion has anomaly of change in structure and or conformation of complexes. As a result, some times we do not observe the normal expected values for Ni^{2+} complexes. Copper has a single s electron outside the filled 3d shell. This filled d shell is much less effective than a noble gas shell in shielding the 's' electron from nuclear charge. The filled 'd' electrons are involved in metallic bonding. This factor contributes to much more noble character of copper, the effect to make compounds more covalent. Cu^{2+} has greater lattice and solvation energies and hence, higher formation constant for complex of Cu^{2+} ions has been observed. Here out of the three dipositive ions, Cu^{2+} shows highest value of log K_{MAL}^{MA} among the three as per the expectation. In addition to this in case of copper, splitting of d–orbitals is taking place in two phases. The second phase is known as John–Tellar distortion. This John–Tellar distortion also accounts for extra stability of the Cu^{2+} complexes. Ni^{2+} complexes with oxine and vitamin U is slightly more stable than corresponding [Cu^{2+}–oxine–vitamin U] complex (e.g., Ni^{2+} : log K_{MAL}^{MA} = 6.25 at 25°C and 6.32 at 35°C, where as Co^{2+}, : log K_{MAL}^{MA} = 6.15 at 25°C and 6.25 at 35°C) due to lower size.

It is very interesting to compare the formation constant values of '4f' and '5f' elements i.e., La and Th. Thorium is forming more stable complexes than lanthanum. The formation constants of '3d' and '4f' are very close to each other[14].

The value of mixed ligand formation constants can be explained on the basis of special behaviour of oxine. Beside that, there is also π–bond formation by the back donation of electrons from M $\rightarrow$ N. The $d\pi$–$p\pi$ interaction has been observed in metal–oxine complexes. The N $\rightarrow$ M σ–bonding, there exists strong M $\rightarrow$ N π–interaction due to back donation of electrons from metal $d\pi$ orbital to the vacant delocalised π–orbitals on the oxine molecule. The presence of M $\rightarrow$ N π–bond has been confirmed by various investigations[15, 16].

As a result of π–interaction in $M \rightarrow N$ bond, the concentration of electrons around the metal in $[M(\text{oxine})]^{2+}$ complex does not increase significantly and electronegativity of the metal ion in $[M(\text{oxine})]^{2+}$ remains the same as in $[M(H_2O)]^{2+}$ even in presence of higher concentration of ligand. So it is expected that log K_{MAL}^{MA} should be nearly equal to log $K_{ML_1}^{MA}$. In present study, vitamin U was found to be of bidentate nature, the dissociation of –COOH group brings induction effect, which reduces the dissociation of –NH$_2$ group and makes it more ligating.

The negative value of free energy (ΔG) in all cases indicate that the reaction proceeds spontaneously. The positive value of enthalpy (ΔH) in all case indicate that the complexation reaction is endothermic while, ΔS values also favour chelate formation and stability to the complexes, due to liberation of water molecules from the ion accompanied complexation. This might be due to substitution of solvent molecule attached to the metal ion by the ligand resulting in releasing of these solvent molecules[16].

The ternary complexes of Cr^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, with oxine and vitamin U ligand have been studied to determine their stability and it has been observed that the order of the stability is governed by various factors like stereochemistry, charge on metal ion, electronegativity, nature of metal ion and ligand. The first transition series is selected by nature in various biochemical processes and hence, these data may prove useful in the study of various biochemical reactions.

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