"STUDY ON FORMATION OF SOME MIXED LIGAND TERNARY METAL CHELATES IN SOLUTION"

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ABSTRACT: Metal chelates plays very significant role in our society in medicinal, industrial, analytical, with various other fields and their formation as well as behaviour towards our daily life may be completed with the interaction of metal ions and chelating ligands with the help of some special chemical analysis.

KEYWORDS: Chelating ligand, Potentiometric analysis, SCOGS, ORIGIN.

INTRODUCTION:

The chelating ligand must be of low toxicity and not metabolized so as to persist on changes in the biological system to perform their scavenging functions due to their interaction with metal ions to form metal chelates or dislodging the bound metals and excreting these as soluble chelates from the system. The chelating ligand binds single metal ion and form a heterocyclic ring structure, and the complex compound itself is termed as metal chelate which are of biological[1]analytical[2] industrial[3,4,] and medicinal[5] importance. Metal chelates include substances such as hemoglobin, haemocyanin, myoglobin, vitamin B_{12}, chlorophyll, nucleic acid and various enzymes.[6]

MATERIALS AND EXPERIMENTAL PROCEDURES

Here we studied some binary and ternary complexes specially the ternary complexes in two different ratios (1:1:1) and (1:2:1).

Among the materials which are used in this work, the analytical reagent sodium nitrate plays an important role in this experiment A 0.01 M solution of sodium nitrate was prepared. This solution is essential used to maintain the ionic strength which is standardized by EDTA titrations[7].

A carbonate free sodium hydroxide solution was prepared. For this purpose, a calculated weighed amount of sodium hydroxide (E. Merck) was dissolved in double distilled water in a pyrex flask. The flask was corked and left over for two days. The supernatant solution was rapidly filtered through a sintered bed Jena glass funnel into a polythene bottle, and suitably diluted to give the solution of required strength. Stock solutions (0.01M) of ligand were prepared by constant stirring in double distilled water and had been standardized against a standard oxalic acid solution. The pH measurements were done by an electric digital pH meter (Eutech 501) with a glass electrode supplied with the instrument and working on 220V/50 cycles stabilized by A.C. mains. The pH meter has a reproducibility of ±0.01 pH. The electrode of pH meter was conditioned monthly by saturated Potassium chloride (BDH) solution.

Following solutions were prepared for investigation:

Acid Solution: 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + H_2O

Ligand (A) Solution: 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 2-AHPPA (A) (0.01M) + H_2O

Ligand (B) solution: 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 2,4-DHP (B) (0.01M) + H_2O

Binary Solution: **I** - 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL2-AHPPA (A) (0.01M) + 5mL Hg/ Cd (II) (0.01M) + H_2O

Binary Solution: **II** - 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 2,4-DHP(B) (0.01M) + 5mL Hg /Cd (II) (0.01M) + H_2O

***Ternary Solution*: (1:1:1 = M: A: B):** 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 2-AHPPA(A) (0.01M) + 5mL Hg (II) (0.01M) + 5mL 2,4-DHP (B) (0.01M) + H_2O

***Ternary Solution*: (1:2:1 M:A:B):** 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 10 mL 2-ASA (A) (0.01M) + 5mL Hg (II) (0.01M) + 5mL 2,4-DHP (B) (0.01M) + H_2O

2-AHPPA = 2- amino 3-(4-hydroxyphenyl) propanoic acid, (A)

2-ASA = 2- amino succinic acid, (A) For (1:2:1 M:A:B)

2,4-DHP = 2, 4-dihydroxypyrimidine (B)

RESULT AND DISCUSSION:

The above set of solutions were titrated potentiometrically with the help of Bjerrum's[8] method which was modified by Irving &Rossoti[9,10]. Some research worker[11-14] also had done work in the field of chelation.

Table -1 Hg (II)- 2-AHPPA (A) - 2,4-DHP (B) (1:1:1) Ternary System

Volume of NaOH (mL)	pH			
	A	B	C	D
0.0	2.52	2.74	2.92	3.20
0.2	2.62	2.86	3.14	3.65
0.4	2.73	3.04	3.59	4.48
0.6	2.87	3.37	4.69	5.21
0.8	3.11	5.84	5.77	5.87
1.0	3.65	8.68	6.50	6.71
1.2	9.70	9.20	7.16	8.41
1.4	10.29	9.61	8.04	8.96
1.6	10.53	9.95	8.79	9.35
1.8	10.68	10.20	9.38	9.67
2.0	10.79	10.39	9.86	9.95
2.2	10.88	10.54	10.15	10.16
2.4	10.95	10.66	10.34	10.33
2.6	11.00	10.75	10.47	10.45
2.8	11.05	10.83	10.58	10.55
3.0	11.10	10.89	10.67	10.63
3.2	11.14	10.95	10.74	10.70
3.4		10.99	10.80	10.76
3.6		11.04	10.85	10.82
3.8		11.07	10.90	10.86
4.0		11.10		10.91
4.2				10.95
4.4				10.99

Table- 2 Hg (II)- 2-ASA (A)- 2,4-DHP (B) (1:2:1) Ternary System

Volume of NaOH (mL)	pH			
	A	B	C	D
0.0	2.52	2.61	2.63	2.82
0.2	2.62	2.72	2.77	2.88
0.4	2.73	2.85	2.92	2.94
0.6	2.87	3.02	3.12	3.01
0.8	3.11	3.26	3.40	3.11
1.0	3.65	3.60	3.80	3.23
1.2	9.70	4.20	4.42	3.33
1.4	10.29	8.54	5.36	3.50
1.6	10.53	9.40	6.09	3.70
1.8	10.68	9.89	6.70	3.95
2.0	10.79	10.24	7.41	4.27
2.2	10.88	10.47	9.07	4.76
2.4	10.95	10.63	9.70	6.86
2.6	11.00	10.74	10.04	8.99
2.8	11.05	10.83	10.27	9.45
3.0	11.10	10.91	10.43	9.75
3.2	11.14	10.97	10.56	10.02
3.4			10.66	
3.6			10.74	
3.8			10.81	
4.0			10.87	
4.2			10.92	
4.4			10.97	
4.6			11.00	
4.8			11.04	

Fig.1- Potentiometric titration Curves of 1:1:1 Hg(II)-2-AHPPA(A)- 2,4-DHP (B) System

(A) Acid (B) Ligand(C)Hg (II)-2-AHPPA(D)Hg(II)-2-AHPPA - 2,4-DHP

Fig.2 -Potentiometric titration Curves of 1:2:1 Hg (II)-2-ASA(A) - 2,4-DHP (B) System

(A) Acid (B) Ligand (C) Hg(II)- 2-ASA (D) Hg(II)-2-ASA - 2,4-DHP

Formation of binary complexes:

Hg^{++}+ 2-AHPPA (H_2A) $\rightleftharpoons$ [Hg-2-AHPPA] + $2H^+$

Hg^{++}+ 2,4-DHP (BH^-) $\rightleftharpoons$ [Hg- 2,4- DHP] + H^+.

Hg^{++}+ 2-ASA (H_2A) $\rightleftharpoons$ [Hg-2-ASA] + $2H^+$

***Formation of Ternary complexes* (1:1:1)**

[Hg-2-AHPPA] + BH^- $\rightleftharpoons$ [Hg-2-AHPPA-,2,4- DHP] + H^+

Hg^{++}+ 2-AHPPA (H_2A) +2,4- DHP (BH^-) $\rightleftharpoons$ [Hg-2-AHPPA – 2,4- DHP] + $3H^+$

***Formation of Ternary complexes* (1:2:1)**

[Hg-2-ASA] + BH^- $\rightleftharpoons$ [Hg-2-ASA -,2,4- DHP] + H^+

Hg^{++} + 2-ASA (H_2A) + 2,4- DHP (BH^-) ⇌ [Hg-2--ASA – 2,4- DHP] + $3H^+$

General hydrolytic equilibria :

$Hg^{++} + H_2O \rightleftharpoons Hg(OH)^+ + H^+$

$Hg^{++} + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+$

Study of stability constant of various species:

The equation for stability constants or log ß value ($ß_{p/qrst}$) of the Hg– 2-AHPPA -2,4- DHP (**1:1:1)** ternary species given as:

$p(Hg^{++}) + r(2\text{-AHPPA}) + s(2,4\text{- DHP}) + t(OH) \rightleftharpoons (Hg^{++})_p\,((2\text{-AHPPA})_r\,(2,4\text{- DHP})_s\,(OH)_t$

$$\beta_{p/qrst} = \frac{[(Hg^{++})_p\,(2\text{-AHPPA})_r(2,4\text{- DHP})_s(OH)_t]}{[Hg^{++})]^p[2\text{-AHPPA}]^r\,[2,4\text{- DHP}]^s\,[OH]^t}$$

The equation for stability constants or log ß value ($ß_{p/qrst}$) of the Hg– 2-ASA -2,4- DHP (**1:2:1)** ternary species given as:

$p(Hg^{++}) + r(2\text{-ASA}) + s(2,4\text{- DHP}) + t(OH) \rightleftharpoons (Hg^{++})_p\,((2\text{-ASA})_r\,(2,4\text{- DHP})_s\,(OH)_t$

$$\beta_{p/qrst} = \frac{[(Hg^{++})_p\,(2\text{-ASA})_r(2,4\text{- DHP})_s(OH)_t]}{[Hg^{++})]^p[2\text{-ASA}]^r\,[2,4\text{- DHP}]^s\,[OH]^t}$$

β = stability constant, p = M_1, q = M_2 ,

r = primary ligand, s = secondary ligand, t = hydroxo species.

The stability constant metal chelates were studied by using SCOGS[15-17](Stability constant of generalized species) computer programme and the titration and species distribution curves were sketched with the help of ORIGIN 6.0. another advanced computer programme.

SPECIES DISTRIBUTION CURVES:

Species distribution curves are obtained by plotting percent (%) concentration of the species against pH. The distribution curves are finally sketched by running the computer program ORIGIN 6.0.

- **Hg (II)-2-AHPPA (A) - 2, 4- DHP(B) System** (1:1:1)

In the present system following species are identified:

Protonated ligand species; H_3A, H_2A, HA and HB, Free metal ion species: Hg^{2+} (aq.). Hydroxo species: Hg $(OH)_2$ Binary species: HgA, HgB and Ternary species: Hg AB.

From the distribution curves it is very clear that maximum concentration attaining species is mixed ligand ternary complex Hg AB its maximum concentration is ~ 68% at the pH ~ 9.0. Binary complex of Hg B shows ~ 98% concentration at start of the titration but gradual decreases with increase in pH and now the ternary complex increases gradually from pH ~ 5.8. Another binary complex Hg A shows its maximum concentration ~ 52% at the pH ~ 9.8. Protonated ligand species H_3A, H_2A, HA and HB shows their remarkable presence in this system.

- **Hg (II)- 2-ASA (A) - 2, 4-DHP(B) (1:2:1) System**

For the present system species distribution curve are represented in fig. 4.

In this system following species are identified:

Protonated ligand species; H_3A, H_2A, HA and BH, Free metal ion species: Hg^{2+} (aq.),Hydroxo species: Hg $(OH)_2$. Binary species: Hg A, Hg B and Ternary species: Hg AB.

In this system protonated ligand species shows their remarkable presence.

The binary complex of Hg A exist with concentration ~39.5% at ~4.2 pH range and decreases with raise in pH value. Another binary complex of Hg B exists in good concentration ~ 78% at start of the titration and gradually decreases with increase in pH range. Ternary complex of Hg AB exist with maximum concentration ~ 62 %at higher pH ~ 8.0. Hydroxo species $Hg(OH)_2$ also seen in this system in good concentration.

Fig. 3-Distribution Curves of 1:1:1 Hg(II)- 2-AHPPA (A) -2,4-DHP(B) System (1) Hg^{2+} (2) H_3A (3) H_2A (4) HA(5) BH (6) Hg $(OH)_2$(7)Hg A(8)HgB (9) HgAB

Fig 4 - Distribution Curves of 1:2:1 Hg (II)-2- ASA(A) - 2,4-DHP (B) System

(1) Hg^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6)$Hg(OH)_2$ (7)Hg A (8)HgB (9) HgAB

Overall stability constants and other related constants of binary and ternary complexes for M (II) 2-AHPPA(A) -2,4-DHP(B) (1:1:1) System.

- Proton-ligand formation constant (log β_{00r0t}/ log β_{000st}) of 2-AHPPA - 2,4-DHP at 37 $\pm 1^0$C I = 0.1 $NaNO_3$

Complex	log β_{00r0t}/ log β_{000st}
H_3A	21.35
H_2A	19.18
HA	10.14
BH	9.49

- Hydrolytic constants (log β_{p000t}/ log β_{0q00t}) M^{2+} (aq.) ions.

Complex	Hg
$M(OH)^+$	-3.84
$M(OH)_2$	-6.38

- Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System

Complex	Hg
MA	12.25
MB	13.08

- Metal-Ligand constants (log β_{p0rs0}/ log β_{0qrs0}):Ternary System(1:1:1)

Complex	Hg
MAB	21.82

Overall stability constants and other related constants of binary and ternary complexes for M (II)- 2-ASA(A)- 2,4-DHP(B) (1:2:1) system.

- Proton-ligand formation constant (log β_{00r0t}/ log β_{000st}) of 2-ASA - 2,4-DHP at 37 ± ^{10}C I = 0.1 NaN_{O3}

Complex	log β_{00r0t}/ log β_{000st}
H_3A	15.26
H_2A	13.33
HA	9.63
BH	9.49

- Hydrolytic constants (log β_{p000t}/ log β_{0q00t}) M^{2+} (aq.) ions.

Complex	Hg
$M(OH)^+$	-3.84
$M(OH)_2$	-6.38

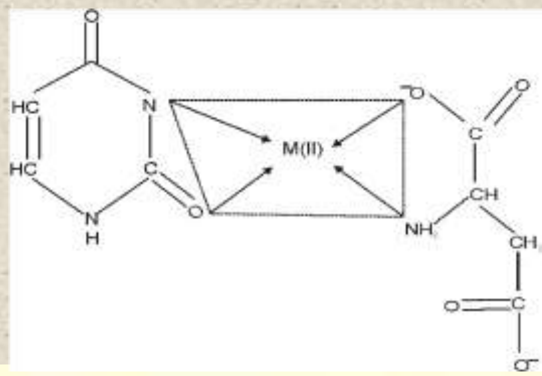
- Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System

Complex	Hg
MA	13.09
MB	13.08

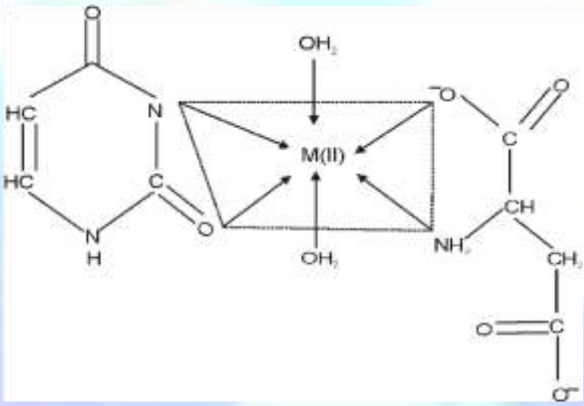
- Metal-Ligand constants (log β_{p0rs0}/ log β_{0qrs0}/) : Ternary System(1:2:1)

Complex	Hg
MAB	21.58

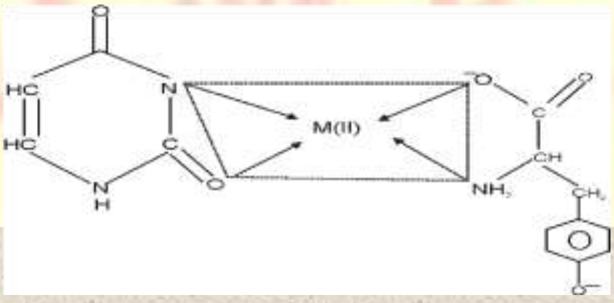
Proposed Ternary Structure;-



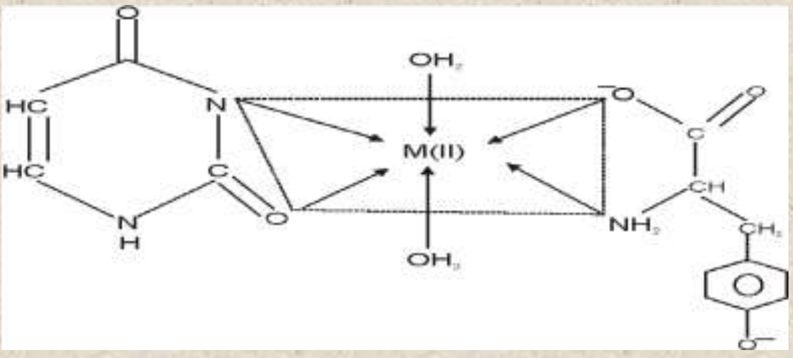
M (II)-2-ASA-2,4-DHP 4- Coordinated



M (II)-2-ASA-2,4-DHP 6- Coordinated



M (II)-AHPPA-2,4-DHP 4- Coordinated



M (II)-AHPPA-2,4-DHP 6- Coordinated

CONCLUSION:

From the above study the fact comes out that the stability constant of ternary metal chelate of 1:2:1 is greater than ternary chelate of 1:1:1 which indicate that the both conditions provide suitable environment to form effective metal chelate having the fruitful values in society. This study also provides a good method for removal of Hg which is hazardous for us.

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