"OVERALL STABILITY CONSTANTS AND OTHER RELATED CONSTANTS OF SOME COMPLEXES IN CO-ORDINATION CHEMISTRY"

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Abstract: The stepwise stability constants and their overall stability constants with related constant like hydrolytic constants have very significant role to understand theformationof species during complexation process and this study wasmade completedby potentiometric titration followed by SCOGS computer programme showing stable complexes in species distribution curves which are a graphical way to know how a complex is formed in aqueous medium.

Keywords: Overall stability constant, Hydrolytic constant,species distribution curves, SCOGS.

Introduction: In coordination chemistry any complex is formed in a specific step and each step has its specific stability value and then an overall stability constant would be calculated with other related constants. In the present paper we study about the complex formed through interaction among ternary complexation in two different ratios of MAB (1:1:1) and (1:2:1) and quaternary complexation of MMABin (1:1:1:) molar ratio.Here we studiedabout thestability constantof some binary, ternary and quaternary compounds of bivalent Pband Hg metal ions with bio ligand 2- amino 3-(4-hydroxyphenyl) propanoic acid (2-AHPPA) which is a non-essential amino acid with a polar side group and a number of studies have found that it would be useful during conditions of stress, cold, fatigue[1] loss of a loved one such as in death or divorce, prolonged work and sleep deprivation[2]and 2- amino succinic acid(2-ASA)acts as a neurotransmitters[3]used as primary ligand A while2,4-dihydroxopyrimidine (2,4-DHP). a pyrimidine base of RNA used as secondary ligandB.

Materials and Procedures:

For our study we prepare some solutions with different ratios as follows:

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

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

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

Ligand (B) solution: III- 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) + *5mL 2-AHPPA* (A) (0.01M) + 5mL Hg/ Pb (II) (0.01M) + H_2O

Binary Solution: II - 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + *5mL 2-ASA (A*) (0.01M) + 5mL Hg/ Pb (II) (0.01M) +

H_2O

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

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

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

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

The concept of stability constant in chemical equilibrium between a metal ion 'M' and a ligand 'L' in gaseous phase was introduced by Abegg and Bodlander[4,5] for a reaction of the type.

$$M_{(g)} + nL_{(g)} ML_{n(g)} \text{ .... (1)}$$

Formation of complex in solution proceeds by the stepwise addition of the ligands to the metal ion, a number of successive equilibria can be formulated. The above equilibrium may generally be written in a more convenient form as,

$$\begin{aligned} M + L &\rightleftharpoons ML \\ ML + L &\rightleftharpoons ML_2 \\ ML_2 + L &\rightleftharpoons ML_3 \\ ML_{n-1} + L &\rightleftharpoons ML_n \end{aligned} \quad \text{........... (2)}$$

From Law of Mass Action,

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\vdots$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad \text{.............. (3)}$$

Where n represents the coordination number of the metal ions, terms in bracket [ ] refers to the activities of different species and K_1, K_2, K_3……….K_n are thermodynamic stepwise stability constant or formation constant.

$$\beta n = \frac{[ML_n]}{[M]\,[L]^n} \qquad \text{……………} \quad (4)$$

where βn (overall stability constant) is the product of stepwise formation constant (K_1, K_2, K_3,…….K_n).

RESULTS AND DISCUSSION

In this work the metal solution were standardized by EDTA titrations[6] while the potentiometric titration were completed with the help of Bjerrum's[7] method modified by Irving & Rossoti Technique[8,9] using an electric digital pH meter (Eutech 501) having a reproducibility of ±0.01. The overall stability constants of investigated complexes were calculated by using SCOGS[10-12] (Stability constant of generalized species) computer programme.Some other research workers[13-18] also studied in this field.

The titration and species distribution curves were sketched by using computer program named as ORIGIN 6.0. Titration curves were plotted by taking pH value of acid, ligand, binary ternary and quaternarycomplexes vs. volume of NaOH and species distribution curves were plotted by taking percent (%) concentration of the species against pH.

Table 1

Pb (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	2.61	3.05
0.2	2.62	2.86	2.84	3.36
0.4	2.73	3.04	3.12	3.89
0.6	2.87	3.37	3.37	4.18
0.8	3.11	5.84	3.54	4.67
1.0	3.65	8.68	3.89	5.38

1.2	9.70	9.20	4.14	6.12
1.4	10.29	9.61	4.36	6.49
1.6	10.53	9.95	4.53	6.87
1.8	10.68	10.20	5.02	7.24
2.0	10.79	10.39	5.29	7.83
2.2	10.88	10.54	5.49	8.43
2.4	10.95	10.66	6.37	8.92
2.6	11.00	10.75	7.04	9.26
2.8	11.05	10.83	7.68	9.41
3.0	11.10	10.89	8.12	9.97
3.2	11.14	10.95	8.49	10.19
3.4		10.99	9.25	10.42
3.6		11.04	10.28	10.56
3.8		11.07	10.47	10.67
4.0		11.10	10.52	10.82
4.2			10.54	10.93

Table 2

Pb (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	2.41	2.99
0.2	2.62	2.72	2.65	3.07
0.4	2.73	2.85	2.70	3.16

0.6	2.87	3.02	3.75	3.27
0.8	3.11	3.26	3.86	3.36
1.0	3.65	3.60	4.93	3.57
1.2	9.70	4.20	5.12	3.76
1.4	10.29	8.54	6.31	3.99
1.6	10.53	9.40	7.56	4.27
1.8	10.68	9.89	8.74	4.69
2.0	10.79	10.24	9.08	5.69
2.2	10.88	10.47	9.38	6.80
2.4	10.95	10.63	10.21	7.67
2.6	11.00	10.74	10.32	8.63
2.8	11.05	10.83	10.63	8.99
3.0	11.10	10.91	10.74	9.27
3.2	11.14	10.97	10.86	9.49
3.4				9.66
3.6				9.83

Table 3

Hg(II)-Pb (II)- 2-ASA (A) - 2,4 –DHP (B) (1:1:1:1) Quaternary**system**

Volume of NaOH (mL)	**pH**				
	A	**B**	**C**	**D**	**E**
0.0	2.52	2.61	2.63	2.48	2.75
0.2	2.62	2.72	2.77	2.61	2.82
0.4	2.73	2.85	2.92	2.73	2.90

0.6	2.87	3.02	3.12	2.87	2.99
0.8	3.11	3.26	3.40	3.05	3.10
1.0	3.65	3.60	3.80	3.29	3.25
1.2	9.70	4.20	4.42	3.60	3.45
1.4	10.29	8.54	5.36	4.03	3.79
1.6	10.53	9.40	6.09	4.62	4.40
1.8	10.68	9.89	6.70	5.32	5.70
2.0	10.79	10.24	7.41	5.91	6.90
2.2	10.88	10.47	9.07	6.50	7.73
2.4	10.95	10.63	9.70	8.63	9.23
2.6	11.00	10.74	10.04	9.35	9.81
2.8	11.05	10.83	10.27	9.75	10.25
3.0	11.10	10.91	10.43	10.04	10.55
3.2	11.14	10.97	10.56	10.25	10.85
3.4			10.66	10.40	10.98
3.6			10.74	10.51	
3.8			10.81	10.61	
4.0			10.87	10.69	
4.2			10.92	10.75	
4.4			10.97	10.81	
4.6			11.00	10.87	
4.8			11.04	10.92	

Titration curves

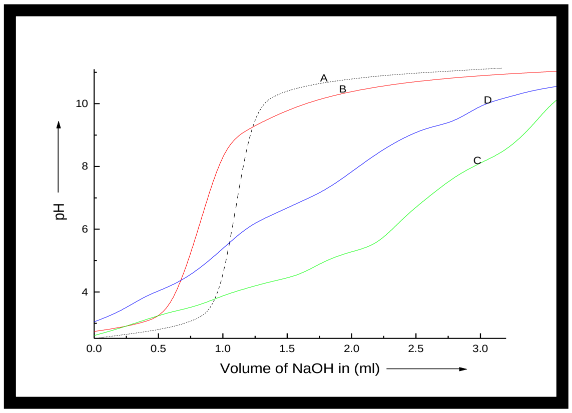


Fig1 - Potentiometric titration Curves of 1:1:1 Pb (II)- 2-AHPPA (A)- 2,4-DHP (B) System

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

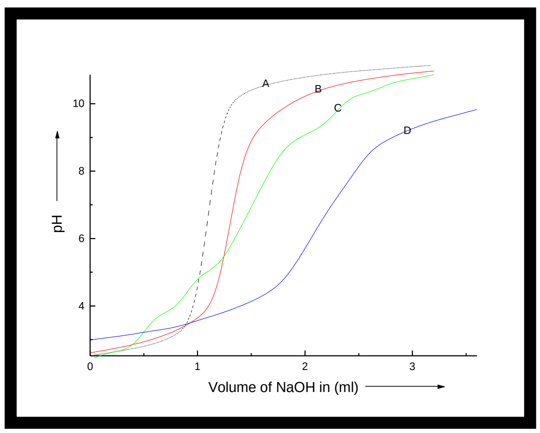


Fig.2- Potentiometric titration Curves of 1:2:1 Pb (II) - 2-ASA (A) - 2,4-DHP (B)System

(A) Acid (B) Ligand (C)Pb(II)- 2-aminosuccinic acid (D) Pb(II)- 2-ASA - 2,4-DHP

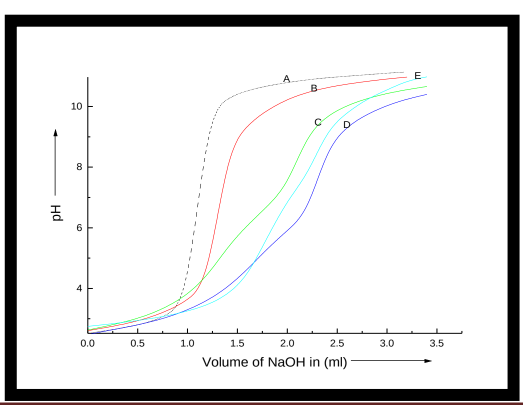


Fig. 3- Titration Curves of 1:1:1:1 Hg (II)-Pb (II) - 2-ASA(A)- 2, 4 –DHP(B) system

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

SPECIES DISTRIBUTION CURVES:

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

For the present system species distribution curves 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: Pb^{2+} (aq.). binary species: Pb A, Pb B

ternary species Pb A B.

In this system binary species PbA shows its maximum concentration very low amount but another binary complex Pb B shows its maximum concentration ~ 98% at beginning of titration which gradually decreases.

In this system ternary complex of PbAB is major species having concentration ~ 84% at higher pH ~ 9.9. In present system protonated ligand species and free metal ion species shows its remarkable presence.

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

For the present system species distribution curve are represented in fig. 5.

In this systemspecies distribution curves reveal the existence of protonated ligand species H_3A, H_2A, HA and BH, free metal ion, binary Pb A, Pb B and ternary complex species Pb AB in the variable concentration profile. Binary complex of Pb A shows its maximum concentration ~ 19% at pH ~ 5.6 while the binary complex of Pb B shows maximum concentration ~ 91% at very start of titration which is gradually decreases with rise in pH .H_2A species have the maximum concentration ~ 70% at the start of titration. H A shows maximum concentration ~ 79% at~ 5.5 pH.The ternary complex shows maximum concentration ~ 88% at the higher pH ~ 9.7.

Hg(II)–Pb (II) –2-ASA(A)- 2, 4–DHP (B)(1:1:1:1) Quaternary System

The fig 6. shows the distribution diagram of present system .In this system Hg^{2+},$Pb^{2+}$$H_2A$, HA, Hg $(OH)_2$,Hg

A, HgB,PbA ,PbB, HgAB, PbAB and Hg Pb AB species were identified.

The ternary complexes of PbAB existed in very good amount attaining maximum concentration ~90% at the ~ 9.7 pH value. Hg AB exit in low amount ~12% at the ~ 9.0 pH. The major species which is quaternary complex of Hg Pb AB attain the maximum concentration ~98% at the ~ 4.8 pH. Binary complex of Hg with ligand B have their existence ~10.0% at the pH ~ 9.4 while the another binary complex Hg A shows low amount ~2.0% at the pH ~ 6.5. Complex PB- A attain maximum concentration ~10% at the pH ~ 8.6 while the Pb B complex attain the maximum concentration ~11% at the ~ 9.2 pH value.

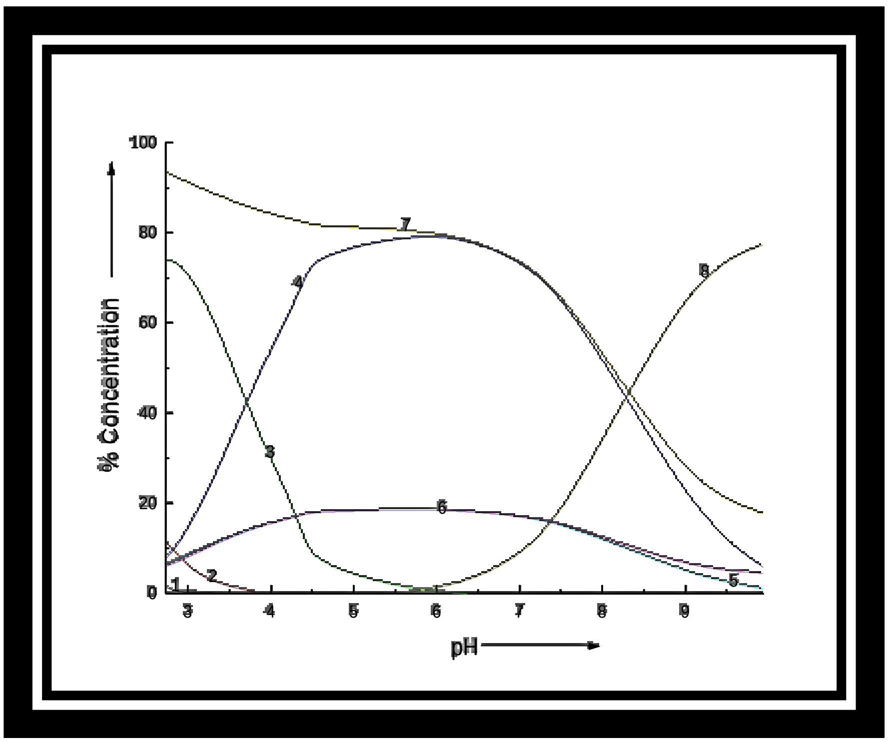


Fig 4 - Distribution Curves of 1:1:1 Pb (II)-2-ASA(A) - 2,4-DHP (B)System

(1) Pb^{2+}(2) H_3A (3) H_2A (4) HA (5) BH (6)Pb A (7)PbB (8) PbAB

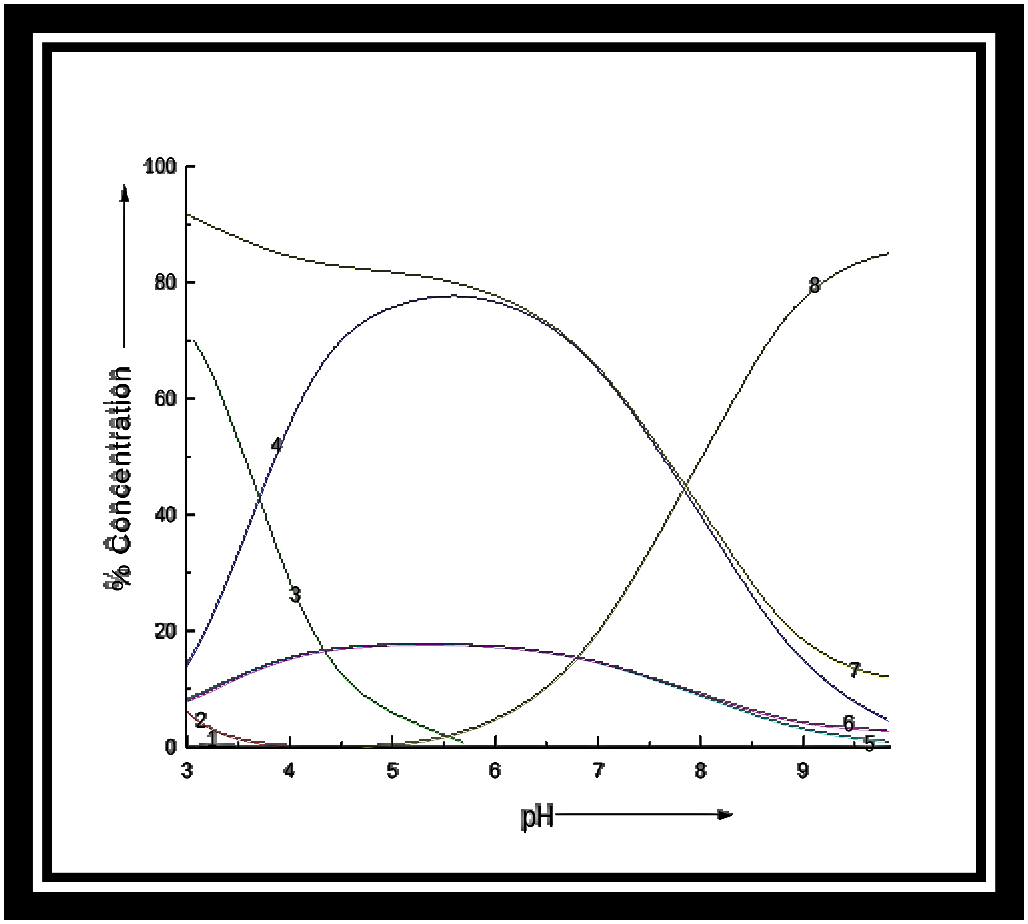


Fig 5- Distribution Curves of 1:2:1 Pb (II)-2-ASA (A) - 2,4-DHP (B) System

(1) Pb^{2+} (2) H_3A (3) H_2A (4) HA (5) HB (6)Pb A (7)PbB (8) PbAB

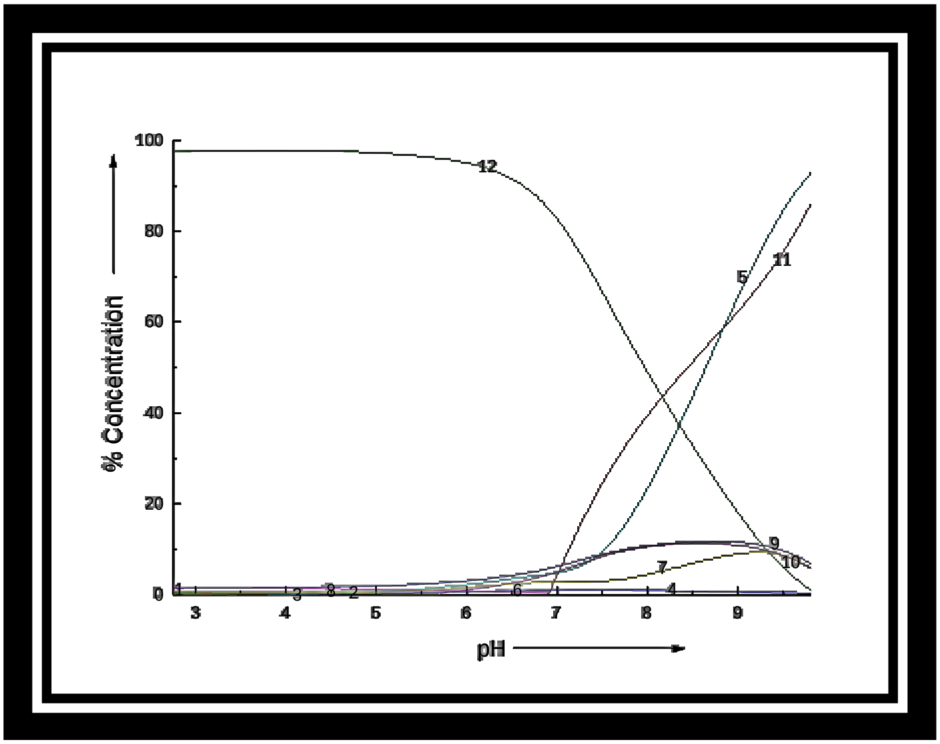


Fig 6- Distribution Curves of1:1:1:1 Hg(II)–Pb (II) –2-ASA(A)- 2, 4–DHP (B) System

(1) Hg^{2+}(II) (2) Pb^{2+}(II) (3) H_2A (4) HA (5)$Hg(OH)_2$(6)Hg A (7)Hg B(8)Pb A(9)Pb B (10)Hg AB (11)Pb A B(12)Hg Pb AB

<u>Equilibria of complex formation</u>:

<u>Formation of Binary Complexes:</u>

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

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

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

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

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

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

<u>Ternary Complex Formed Through Two Ways:</u>

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

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

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

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

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

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

Quaternary complex formed through two ways:

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

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

General hydrolytic equilibria are as follow:

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

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

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

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

Calculation of overall stability constant:

The equation for overall stability constants or log ß value ($ß_{prst}$) of the Pb – 2-AHPPA -2,4-DHP (1:1:1) ternary species given as:

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

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

The overall stability constants or log ß value ($ß_{prst}$) of thePb– 2-ASA -2,4-DHP (1:2:1) ternary species given as:

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

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

The overall stability constants or log ß value ($ß_{prst}$) of the Hg- Pb– 2-ASA -2,4-DHP (1:1:1:1) quaternary species given as:

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

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

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

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

Overall stability constants and other related constants Pb(II) 2-AHPPA(A)-2,4-DHP(B) (1:1:1)system.

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

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

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

Complex	Pb
$M(OH)^+$	-9.84
$M(OH)_2$	-15.54

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

Complex	Pb
MA	4.14
MB	12.77

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

Complex	Pb

MAB	18.48

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

- Proton-ligand formation constant(log β_{00r0t}/log β_{000st}) of 2-ASA - 2,4-DHP at 37 $\pm ^{10}$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 (logβ_{p000t}/ logβ_{0q00t})M^{2+} (aq.) ions.

Complex	Pb
$M(OH)^+$	-9.84
$M(OH)_2$	-15.54

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

Complex	Pb
MA	11.61
MB	12.77

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

Complex	Pb
MAB	18.62

Overall stability constants and other related constants of binary, ternary andquaternarycomplexes forHg (II)- Pb(II) 2-ASA(A)-2,4-DHP(B) system.

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

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

- Hydrolytic constants of M^{2+} (aq.) ions. ($\log\beta_{p000t}/\log\beta_{0q00t}$)

Complex	Hg	Pb
$M(OH)^+$	-3.84	-9.84
$M(OH)_2$	-6.38	-15.54

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

Complex	Hg	Pb
MA	13.09	11.61
MB	13.08	12.77

- Metal-Ligand constants($\log\beta_{p0rs0}/\log\beta_{0qrs0}$) :TernarySystem(1:1:1)

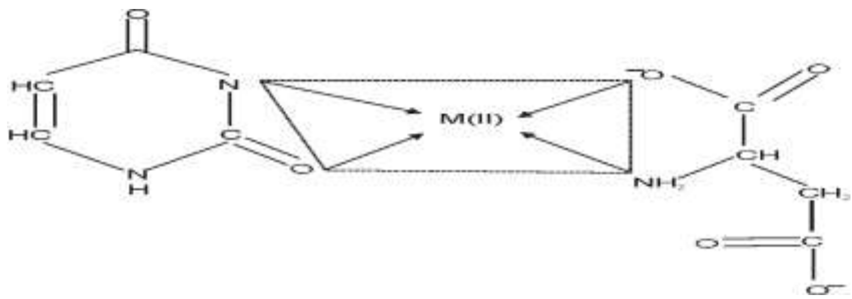
Complex	Hg	Pb

MAB	21.00	18.08

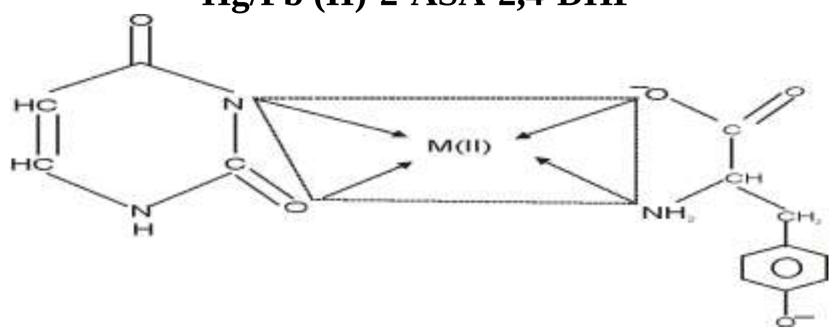
- Metal-Ligand constants(Log $\beta_{pqrst)}$: Quaternary(1:1:1:1) System

Complex	Hg-Pb
M_1-M_2-A-B	29.45

Proposed Ternary Structure;-

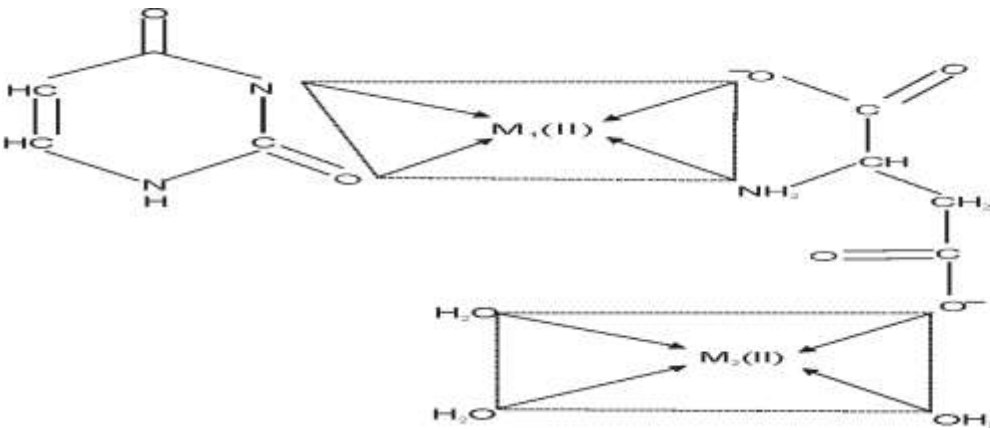


Hg/Pb (II)-2-ASA-2,4-DHP



Hg/Pb (II)-AHPPA-2,4-DHP

Proposed quaternarystructures:



Hg(II)-Pb (II)-2-ASA-2,4-DHP

Conclusion:

From the above discussion it is very clear that the overall stability constant of complexes depend upon all the step wise process which involved in complex formation. The order of overall stability constant of various investigated species follows a trend quaternary species, ternary of 1:2:1, ternary of 1:1:1 and then binary of Hg and Pb with primary as well as secondary ligands which is due to increased number of fused ring and the extra stabilization caused by ligand –ligand interactions.

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