" ANALYSIS OF ELECTROCHEMICAL BEHAVIOUR OF SOME SIGNIFICANT INORGANIC COMPLEXES"

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Abstract: *The electrochemical behavior of any complex provides us various information about the studying complexes and the potentiometry is an important method to analyzing the electrochemical behavior and equilibria of interaction of metal ions with complexing agent where there is a release of hydrogen ions accompanying the complexation reaction and glass electrode furnishes information on the hydrogen ion concentration and thereby on the extent of complex formation.*

Keywords: Electrochemical Behavior, ORIGIN, SCOGS. Potentiometry, Complexing agent.

INTRODUCTION: Inorganic complexes has great significance for humanand covered several field of their life.In the present paper we study and analyze the electrochemical behavior of biologically significant complexes of highly toxic metal divalent mercury and cadmium with four different complexing agent 2- amino 3-(4-hydroxyphenyl) propanoic acid,(2-AHPPA),2-aminosuccnic acid (2-ASA) used in chronic fatigue, enhancing immune system and protectfrom neural and brain disorder while the 5-methyl uracil(5-MU) is the first pyrimidine to be purified from a natural source, and the 2, 4-dihydroxypyrimidine (2,4-DHP)isa planar, unsaturated pyrimidine base which was isolated from the hydrolysis of yeast nuclein[1]that was found in bovine thymus and spleen, herring sperm, and wheat germ.[2] and have the ability to absorb the light[3].

MATERIALS AND EXERIMENTAL PROCEDURES:

In the present investigations we study the electrochemical behaviorof several binary and ternary systems bypH-metry using Bjerrum's[4]method which was modified by Irving & Rossoti[5-6] and pH meter having a reproducibility of ±0.01 with a glass electrodecalibrated with buffer solutions of pH (4.0) and pH (9.2)while the standardization were done with the help of EDTA titration[7] procedure. An immense amount of equilibrium data is available in different volumes published by Martell[8,9]and Smith[10].

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Solutions for Study of Electrochemical Behavior of Various Species:

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

Ligand (B) solution*:* 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL – 5-MU (B) (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 Cd (II) (0.01M) + H_2O

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

***Binary Solution:*III -** 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 5-MU (B) (0.01M) + 5mL Cd (II) (0.01M) + H_2O

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

***Ternary Solution*: (1:1:1):** 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL2-AHPPA (A) (0.01M) + 5mL Cd (II) (0.01M) + 5mL 5-MU (B) (0.01M) + H_2O

***Ternary Solution*: (1:2:2):** 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL2-ASA (A) (0.01M) + 5mL Hg (II) (0.01M) + 5mL 2,4-DHP (B) (0.01M) + H_2O

***RESULTS AND DISCUSSION*:**

The above set of solutions were treated through potentiometric technique of analysis and after aimed study thetitration curves were plotted by taking pH value of acid, ligand, binary and ternary complexes vs. volume of NaOH and species distribution curves were plotted by taking percent (%) concentration of the species against pH and the stability constant have been studied through SCOGS[11-13](Stability constant of generalized species) computer programme andORIGIN 6.0 was used for graphical representation of all investigated species.

Table -1

Cd (II)-2-AHPPA (A) - 5-MU (B) (1:1:1) System

Volume of NaOH (mL)	**pH**			
	A	**B**	**C**	**D**
0.0	2.52	2.74	2.88	3.59
0.2	2.62	2.86	3.05	7.10
0.4	2.73	3.04	3.32	8.10
0.6	2.87	3.37	4.18	8.48
0.8	3.11	5.84	7.79	8.86
1.0	3.65	8.68	8.47	9.16
1.2	9.70	9.20	8.93	9.34
1.4	10.29	9.61	9.17	9.48
1.6	10.53	9.95	9.38	9.62
1.8	10.68	10.20	9.61	9.78
2.0	10.79	10.39	9.84	9.96
2.2	10.88	10.54	10.06	10.16
2.4	10.95	10.66	10.27	10.34
2.6	11.00	10.75	10.40	10.52
2.8	11.05	10.83	10.57	10.67
3.0	11.10	10.89	10.72	10.79
3.2	11.14	10.95	10.85	10.90
‘3.4		10.99	10.95	11.00
3.6		11.04	11.03	
3.8		11.07	11.10	
4.0		11.10	11.17	

Table -2

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

Volume of NaOH (mL)	pH			
	A	B	C	D
0.0	2.52	2.61	2.63	2.84
0.2	2.62	2.72	2.77	2.87
0.4	2.73	2.85	2.92	2.91
0.6	2.87	3.02	3.12	2.96
0.8	3.11	3.26	3.40	3.00
1.0	3.65	3.60	3.80	3.06
1.2	9.70	4.20	4.42	3.12
1.4	10.29	8.54	5.36	3.19
1.6	10.53	9.40	6.09	3.26
1.8	10.68	9.89	6.70	3.36
2.0	10.79	10.24	7.41	3.46
2.2	10.88	10.47	9.07	3.58
2.4	10.95	10.63	9.70	3.73
2.6	11.00	10.74	10.04	3.89
2.8	11.05	10.83	10.27	4.02
3.0	11.10	10.91	10.43	4.24
3.2	11.14	10.97	10.56	4.52
3.4			10.66	5.00
3.6			10.74	6.74
3.8			10.81	6.85
4.0			10.87	7.15
4.2			10.92	7.26
4.4			10.97	7.49
4.6			11.00	
4.8			11.04	

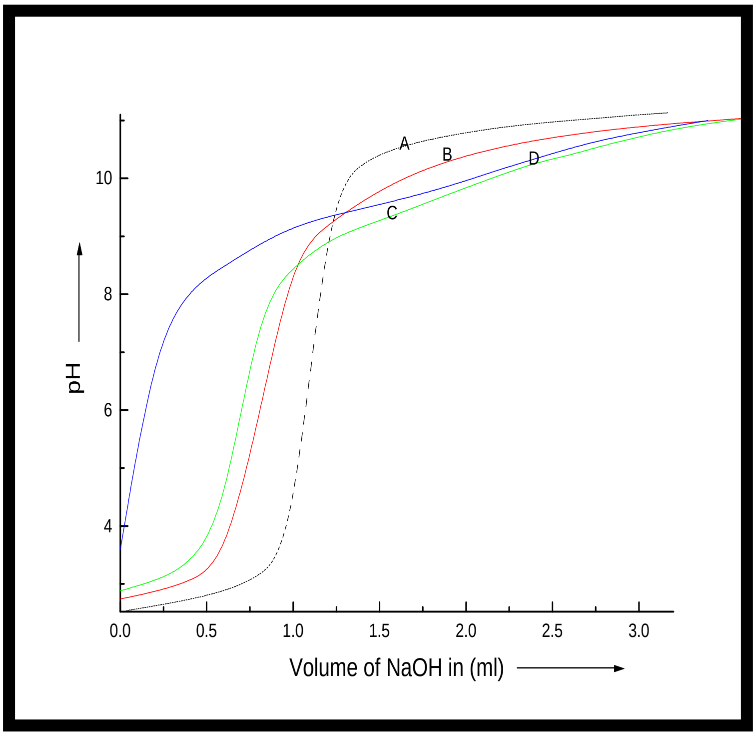


Fig. 1- Potentiometric titration Curves of 1:1:1 Cd (II) - 2-AHPPA(A)- 5-MU(B) System

(A) Acid (B) Ligand (C) Cd(II)- 2-AHPPA (D)Cd(II)- AHPPA -5-MU

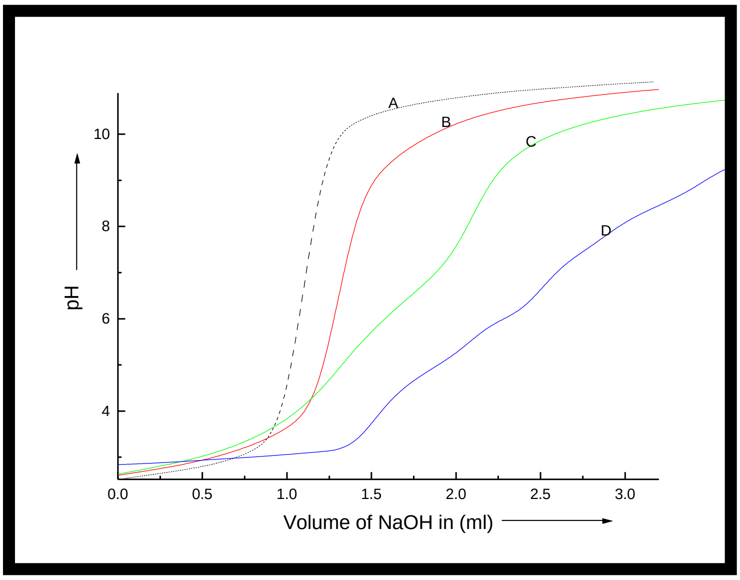


Fig. 2- Potentiometric titration Curves of 1:2:2 Hg (II) - 2-ASA (A)- 2, 4-DHP (B)System

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

Cd (II)- 2-AHPPA (A)-5-MU (B)(1:1:1) System

For the present system species distribution curves were given in fig.3. and the major complex is ternary complex of CdAB having the maximum concentration of ~ 98% at the pH ~ 9.7. The curve shows that binary complex of CdB attains the maximum concentration ~ 94% at start of the titration which gradually decreases with increase in pH value. Protonated ligand species H_3A, H_2A, HA and BH are present in good concentration among these H_2A have maximum concentration ~ 96% at start of the titration. Hydroxo species $Cd(OH)_2$ also seen in this system.

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

From the species distribution curves which is given in fig- 4 it is clear that the binary complex of Hg A exist in concentration ~ 20% at pH ~3.3. Another binary complex Hg B shows its concentration ~ 57% at the pH ~3.0. and the ternary complex of Hg AB exist with higher value having maximum concentration ~ 92% at higher pH ~ 7.3. Protonated ligand species H_3A, H_2A, HA and BH shows their remarkable presence. Hydroxo species also existed in this system.

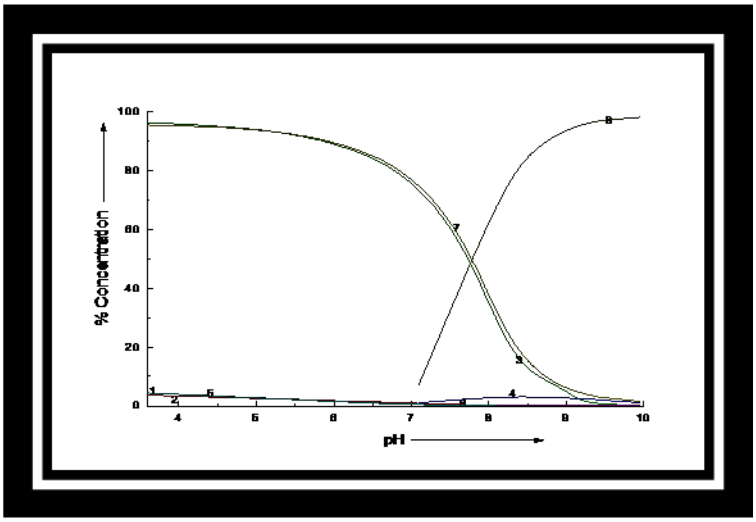


Fig-3-Distribution Curves of (1:1:1) Cd(II)-2-AHPPA(A) - 5-MU(B) System
(1) Cd^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6)$Cd(OH)_2$ (7)Cd B (8) Cd AB

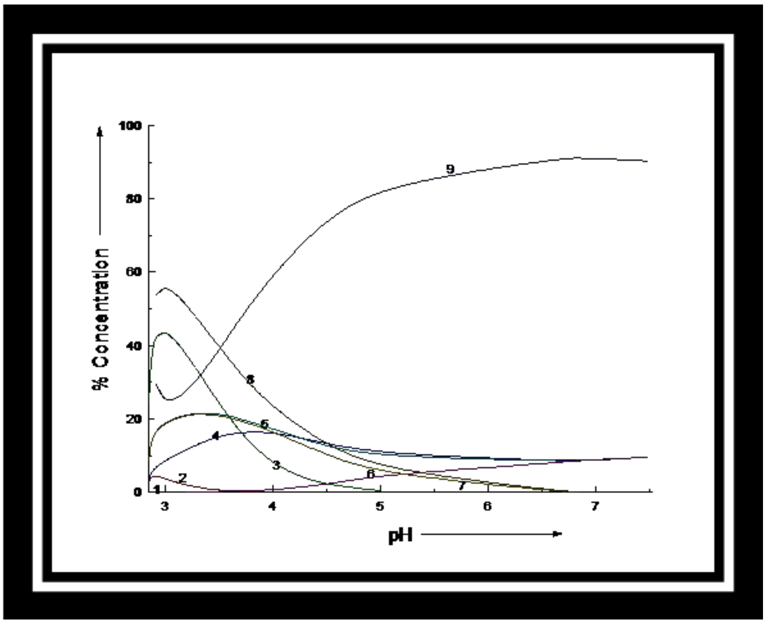


Fig 4-Distribution Curves of (1:2:2)Hg (II)-2-ASA (A) -2,4-DHP (B) System
(1) Hg^{2+}(2) H_3A (3) H_2A (4) HA (5) BH (6)$Hg(OH)_2$ (7)Hg A (8)HgB (9) HgAB

Formation of binary complexes:

Cd^{++}+ 2-AHPPA (H_2A) ⇌ [Cd-2-AHPPA] + $2H^+$

Cd^{++}+ 5-MU (BH^-) ⇌ [Cd-, 5-MU] + H^+

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

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

Formation of Ternary complexes:

[Cd-2-AHPPA] + BH^- ⇌ [Cd-2-AHPPA-,5-MU] + H^+

Cd^{++}+ 2-AHPPA (H_2A) + 5-MU (BH^-) ⇌ [Cd-2-AHPPA –5-MU] + $3H^+$

[Hg-2-ASA] + BH^- ⇌ [Hg-2-ASA-,2,4-DHP + H^+

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

The equation for stability constants or log ß value ($ß_{p/qrst}$) of **(1:1:1)**Cd – 2-AHPPA - 5-MU ternary species given as:

$$p(Cd^{++}) + r(2\text{-AHPPA}) + s(5\text{-MU}) + t(OH) \rightleftharpoons (Cd^{++})_p((2\text{-AHPPA})_r(5\text{-MU})_s(OH)_t$$

$$\beta_{p/qrst} = \frac{[Cd^{++})_p(2\text{-AHPPA})_r(5\text{-MU})_s(OH)_t]}{[Cd^{++})]^p[2\text{-AHPPA}]^r[5\text{-MU}]^s[OH]^t}$$

The equation for stability constants or log ß value ($ß_{p/qrst}$) of**(1:2:2)**Hg – 2-ASA -2,4-DHPternary 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,r = primary ligand, s = secondary ligand, t= hydroxo species.

Overall stability constants and other related constants of binary and ternary complexes for Cd (II) 2-AHPPA(A) - 5-MU(B) (1:1:1) system.

- Proton-ligand formation constant ($\log\beta_{00r0t}$/ $\log\beta_{000st}$)of 2-AHPPA - 5-MU at 37 ± 1^0C I = 0.1 $NaNO_3$

Complex	**log β_{00r0t}/ log β_{000st}**
H_3A	21.35
H_2A	19.18
HA	10.14
BH	9.94

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

Complex	**Cd**
$M(OH)^+$	-6.89
$M(OH)_2$	-14.35

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

Complex	**Cd**
MA	3.57
MB	11.33

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

Complex	**Cd**
MAB	16.95

Overall stability constants and other related constants of binary and ternary complexes for Hg(II) 2-ASA (A)-5-MU(B) (1:2:2) system.

- Proton-ligand formation constant (log β_{00r0t}/ log β_{000st}) of 2-ASA - 5-MU at 37 $\pm 1^0$C, I = 0.1 $NaNO_3$

Complex	log β_{00r0t}/ log β_{000st}
H_3A	15.26
H_2A	13.33
HA	9.63
BH	9.94

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

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

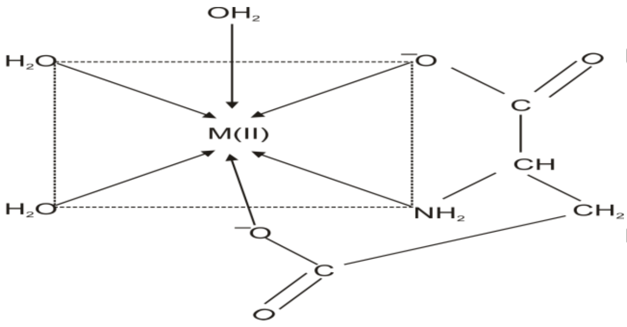
- Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{p00s0}/ log β_{0q0s0}) Binary System

Complex	Hg
MA	13.09
MB	13.45

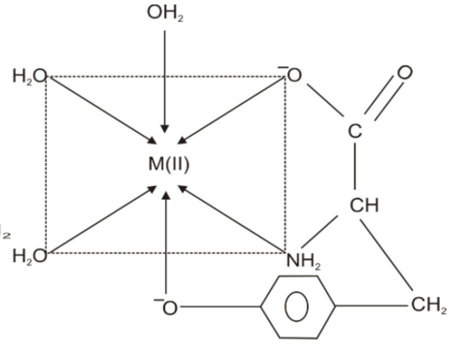
- Metal-Ligand constants (logβ_{p0rs0}/ logβ_{0qrs0}/) : Ternary System(1:2:2)

Complex	Hg
MAB	21.85

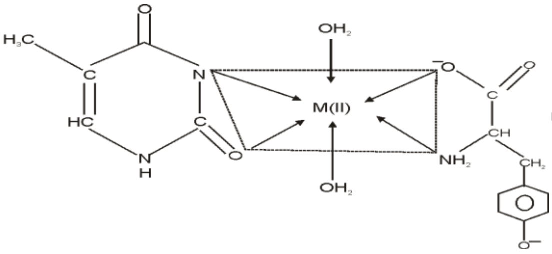
Proposed Structure of Binary and Ternary Complexes:



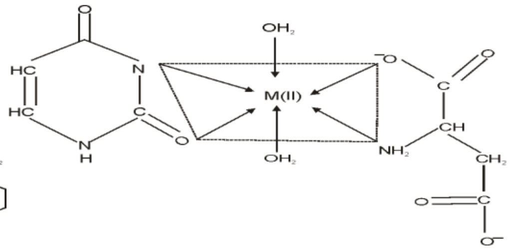
Hg (II)-2-ASA



Cd (II)-AHPPA



Cd (II)-2-AHPPA-5-MU



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

CONCLUSION:

From the above study we can say that potentiometric technique of analysis gives us most of the information about the metal-ligand interaction and formation of various binary, ternary,protonated ligand species H_3A, H_2A, HA, BH, monohydroxo and dihydroxospecies andequilibriaas well as electrochemical behavior of investigated inorganic complexes.

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