

“ 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 human and 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-aminosuccinic acid (2-ASA) used in chronic fatigue, enhancing immune system and protect from 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) is a planar, unsaturated pyrimidine base which was isolated from the hydrolysis of yeast nuclein¹ that was found in bovine thymus and spleen, herring sperm, and wheat germ.² and have the ability to absorb the light³.

MATERIALS AND EXPERIMENTAL PROCEDURES:

In the present investigations we study the electrochemical behavior of several binary and ternary systems by pH-metry using Bjerrum's⁴ method which was modified by Irving & Rossotti⁵⁻⁶ and pH meter having a reproducibility of ± 0.01 with a glass electrode calibrated with buffer solutions of pH (4.0) and pH (9.2) while the standardization were done with the help of EDTA titration⁷ procedure.

An immense amount of equilibrium data is available in different volumes published by Martell^{8,9} and Smith¹⁰.

Solutions for Study of Electrochemical Behavior of Various Species:

Acid Solution: 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + H₂O

Ligand (A) Solution: 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-AHPPA (A) (0.01M) + H₂O

Ligand (A) Solution: 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-ASA (A) (0.01M) + H₂O

Ligand (B) solution: 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 5-MU (B) (0.01M) + H₂O

Ligand (B) solution: 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2,4-DHP (B) (0.01M) + H₂O

Binary Solution: I - 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-AHPPA (A) (0.01M) + 5mL Cd (II) (0.01M) + H₂O

Binary Solution: II - 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-ASA (A) (0.01M) + 5mL Hg (II) (0.01M) + H₂O

Binary Solution: III - 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 5-MU (B) (0.01M) + 5mL Cd (II) (0.01M) + H₂O

Binary Solution: IV - 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2,4-DHP (B) (0.01M) + 5mL Hg (II) (0.01M) + H₂O

Ternary Solution: (1:1:1): 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-AHPPA (A) (0.01M) + 5mL Cd (II) (0.01M) + 5mL 5-MU (B) (0.01M) + H₂O

Ternary Solution: (1:2:2): 5mL NaNO₃ (1.0M) + 5mL HNO₃ (0.02M) + 5mL 2-ASA (A) (0.01M) + 5mL Hg (II) (0.01M) + 5mL 2,4-DHP (B) (0.01M) + H₂O

RESULTS AND DISCUSSION:

The above set of solutions were treated through potentiometric technique of analysis and after aimed study the titration 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 SCOGS¹¹⁻¹³ (Stability constant of generalized species) computer programme and ORIGIN 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	

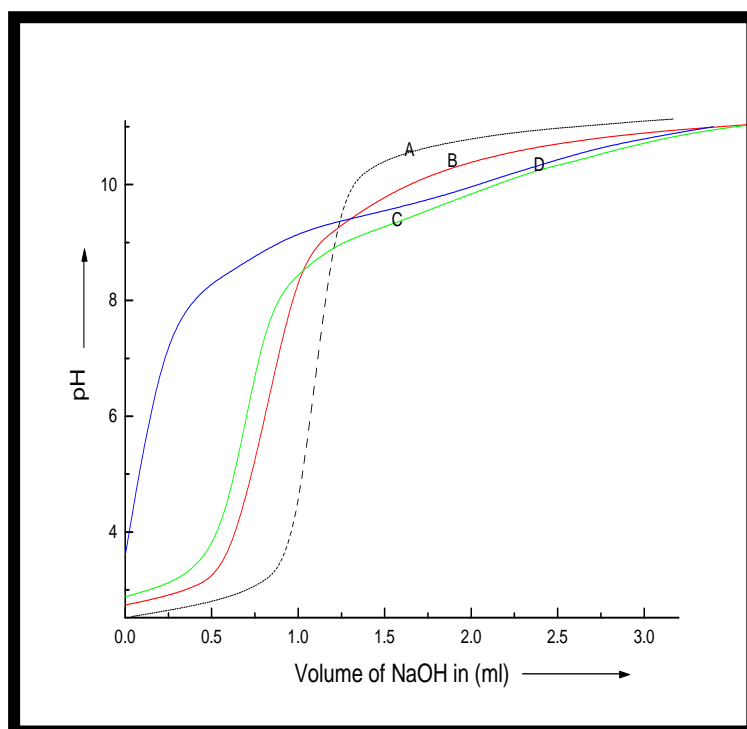


Fig. 1- Potentiometric titration Curves of 1:1:1 Cd (II) - 2-AHPPA(A)- 5-MU(B) System

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

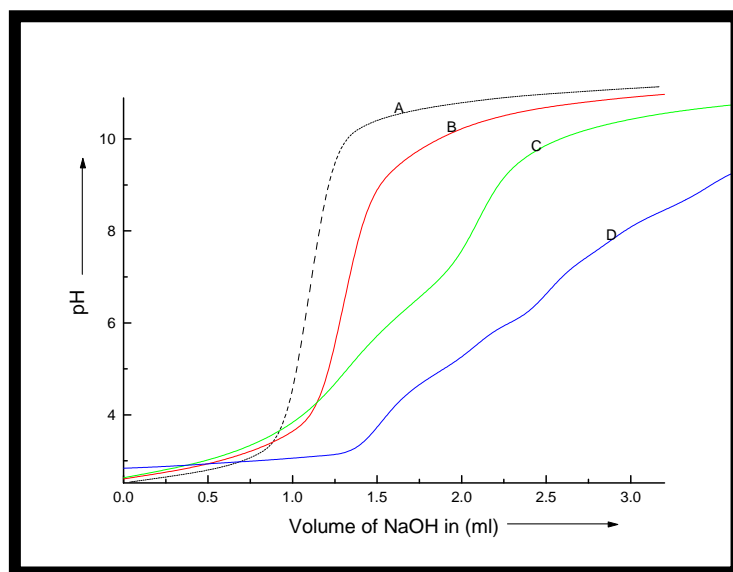


Fig. 2- Potentiometric titration Curves of 1:2:2 Hg (II) - 2-ASA (A)- 2, 4-DHP (B)System

(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 $\sim 96\%$ at start of the titration. Hydroxo species $\text{Cd}(\text{OH})_2$ 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 $\sim 20\%$ at pH ~ 3.3 . Another binary complex Hg B shows its concentration $\sim 57\%$ at the pH ~ 3.0 . and the ternary complex of Hg AB exist with higher value having maximum concentration $\sim 92\%$ 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.

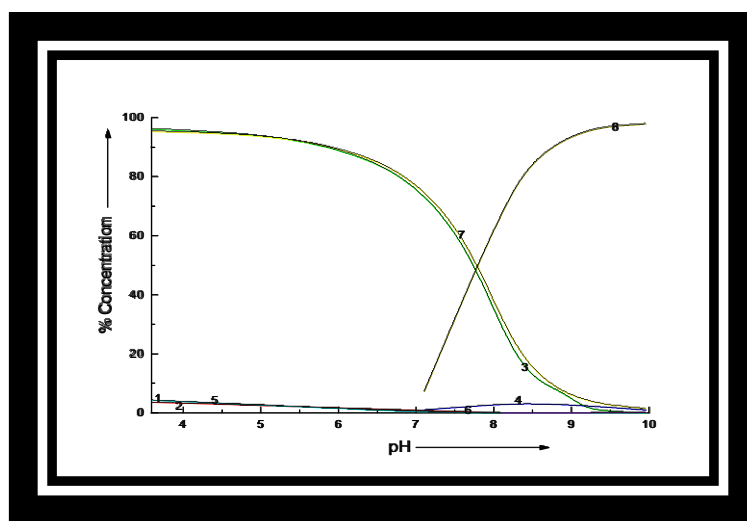


Fig-3-Distribution Curves of (1:1:1) Cd(II)-2-AHPPA(A) - 5-MU(B) System

(1) Cd^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6) $\text{Cd}(\text{OH})_2$ (7) Cd B (8) Cd AB

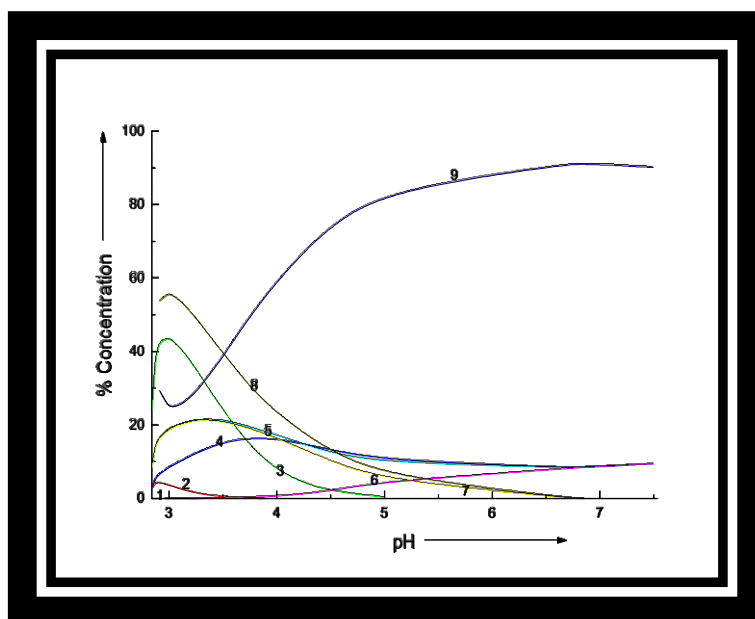
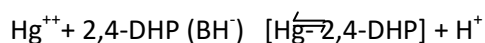
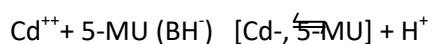


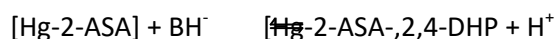
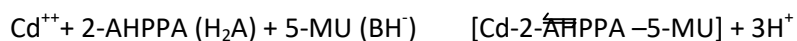
Fig 4-Distribution Curves of (1:2:2)Hg (II)-2-ASA (A) -2,4-DHP (B) System\

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

Formation of binary complexes:



Formation of Ternary complexes:



The equation for stability constants or log β value (β_{pqrst}) of (1:1:1)Cd – 2-AHPPA – 5-MU ternary species given as:

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

$$\beta_{pqrst} = \frac{[\text{Cd}^{++}]^p (2\text{-AHPPA})^r (5\text{-MU})^s (\text{OH})^t}{[\text{Cd}^{++}]^p [2\text{-AHPPA}]^r [5\text{-MU}]^s [\text{OH}]^t}$$

The equation for stability constants or log β value (β_{pqrst}) of (1:2:2)Hg – 2-ASA – 2,4-DHP ternary species given as:

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

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

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 $37 \pm 1^\circ\text{C}$ $I = 0.1$ NaNO_3

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

BH	9.94

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

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

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

Complex	Cd
MA	3.57
MB	11.33

- Metal-Ligand constants ($\log \beta_{p0rs0} / \log \beta_{0qrs0}$): 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 ($\log \beta_{00r0t} / \log \beta_{000st}$) of 2-ASA - 5-MU at $37 \pm 1^\circ\text{C}$, $I = 0.1$ NaNO_3

Complex	$\log \beta_{00r0t} / \log \beta_{000st}$
H ₃ A	15.26
H ₂ A	13.33
HA	9.63
BH	9.94

- Hydrolytic constants ($\log \beta_{p000t} / \log \beta_{0q00t}$) M²⁺ (aq.) ions.

Complex	Hg
M(OH) ⁺	-3.84
M(OH) ₂	-6.38

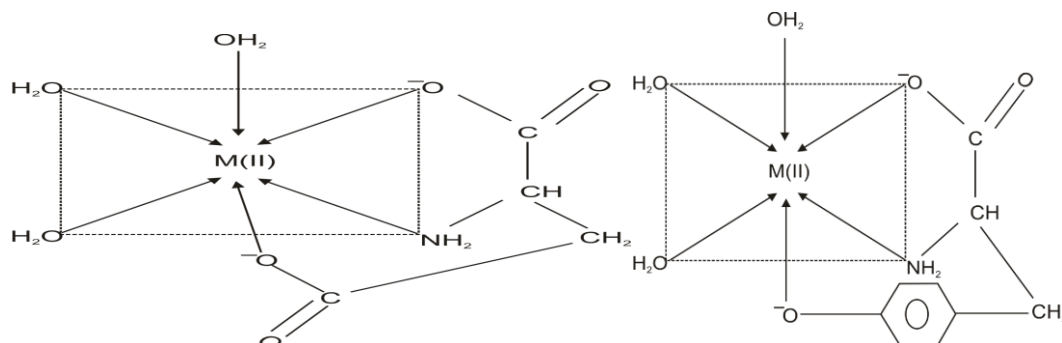
- Metal-Ligand constants ($\log \beta_{p0r00} / \log \beta_{0qr00} / \log \beta_{p00s0} / \log \beta_{0q0s0}$) Binary System

Complex	Hg
MA	13.09
MB	13.45

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

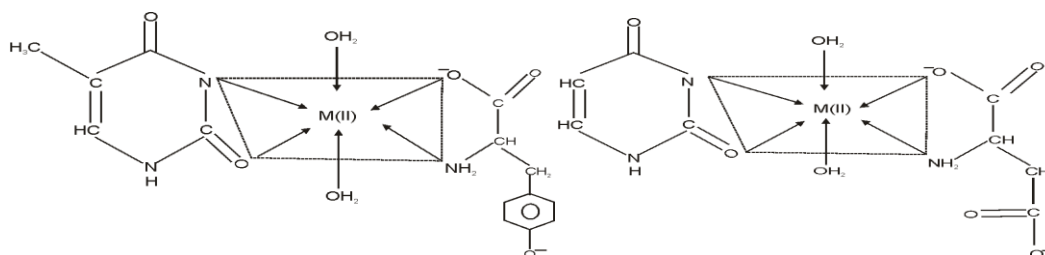
Complex	Hg
MAB	21.85

Proposed Structure of Binary and Ternary Complexes:



Cd (II)-AHPPA

Hg (II)-2-ASA



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 and equilibria as well as electrochemical behavior of investigated inorganic complexes.

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