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Complexation Behavior and Stability Order of Mixed Ligand Ternary Complexes of Hg (II), Pb (II) and Cd (II) with 2- Aminosuccinic Acid and 2,4- dihydroxopyrimidine.

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ABSTRACT

Mixed ligand ternary complexes of Hg(II) ,Pb(II) and Cd(II) has been investigated with 2-Aminosuccinic Acid (2-ASA) and 2,4- dihydroxopyrimidine (2,4-DHP) at silver-silver chloride electrode by the potentiometric technique. The stability constants of Hg(II) -2- Aminosuccinic Acid –2,4- dihydroxopyrimidine, Pb(II)-2- Aminosuccinic Acid–2,4-dihydroxopyrimidine and Cd(II)–2-Aminosuccinic Acid –2,4-dihydroxopyrimidine were determined using SCOGS computer programme and the complex formation were elucidated with the aid of speciation curves. The molar ratio of ternary complexes were kept as 1:1:1 and respectively.

Keywords: Potentiometric Studies, Ligands, SCOGS, Speciation Curves.

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INTRODUCTION

The metal complexes of polydentate ligands have provided both coordination chemist and biochemist with grist for their experimental mills for a long time. Polydentate ligand goes to formation of one or more rings. The resulting structures have been called chelate rings or simple chelates by Morgan and Drew.[1] Cyclic polydentate ligands(Macrocyclic Compound) have attracted increasing interest owing to their role in the under-standing of molecular processes occurring in biochemistry, catalysis and coordination chemistry.[2-5] Complexation of metal ions of biological importance with amino acid, small peptides and their derivatives are of great significance as these serve as models for many complex metal amino acid equilibria occurring in enzymatic processes .Two or more donor atoms of a ligand bind single metal ion and form a heterocyclic ring structure, it is said to be a chelating ligand and the complex compound itself is termed as metal chelate.The metal chelates play an important role in various field of biological[6]analytical[7] industrial[8,9,]and medicinal[10] importance. Metal ion complex formations are among the prominent interaction in nature. 2- ASA combines with other amino acids to form molecules that absorb toxins and remove them from the blood stream. This amino acid acts as a neurotransmitter[11]or neuromodulator. This paper deals with the investigation of Hg(II) Pb(II) and Cd(II) complexes with 2- ASA, and 2,4-DHP.

EXPERIMENTAL

All the solutions were prepared in double distilled water. Potentiometric titrations of each ligand with standard carbonate free sodium hydroxide were carried out with an electric digital pH meter (Century-model CP901-S) with a glass electrode at 37 ± 1^0C and I = 0.1M $NaNO_3$. Relatively low concentrations of metals and ligands are used. A stream of purified nitrogen was passed through the solutions throughout the titration. All the metal salts used were of Analar Grade and were standardized volumetrically by titration with the disodium salt of EDTA is presence of suitable indicators, as described by Schwarzenbatch[12]. For all the binary, ternary and quaternary systems, following solution mixture have been titrated against standardized NaOH (O.01M) solution, keeping the total volume 50.0 ml in each case:

- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2,4-DHP (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Hg(II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Pb (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2,4-DHP (0.01M) + 5ml Hg (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2,4-DHP (0.01M) + 5ml Pb (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2,4-DHP (0.01M) + 5ml Cd (II) (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Hg(II)(0.01M) + 5ml 2,4-DHP (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Pb(II)(0.01M) + 5ml 2,4-DHP (0.01M) + H_2O
- 5ml $NaNO_3$(1.0M) + 5ml HNO_3(0.02M) + 5ml 2-ASA (0.01M) + 5ml Cd(II)(0.01M) + 5ml 2,4-DHP (0.01M) + H_2O

RESULTS AND DISCUSSION

The ligand 2-ASA behaves as a tridentate ligand, coordinating through a nitrogen and two carboxyl oxygen atoms. The secondary ligand 2,4-DHP functions as a monodentate ligand. Proton ligand stability constants obtained for both the ligand are presented in the given table. In this study 1:1 (M:A), 1:1 (M:B) binary and 1:1:1 (M:A:B) ternary mixture have been used to ensure the exclusive formation of the MA, MB and M AB, complex, considering protonation constants of the ligand and hydrolytic constants of the M (II) aqueous ions.

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Titration Curves

The pH titration curves for the 1:1:1 ternary complex were drawn by plotting pH vs. volume of alkali.. The pH titration curves are finally sketched by running the computer program ORIGIN 4.0.Each lines of the curve were denoted by alphabetic word which are A, B, C, and D. In the curves, "A" represent the Acid, "B" represent the Ligand "C" represent the binary complex and "D" represent the mixed ligand ternary complex.

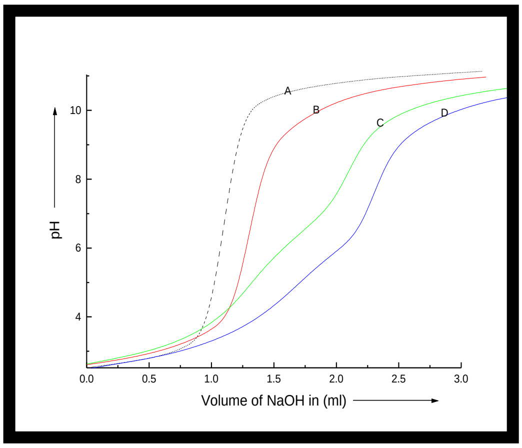

Fig.1. Titration Curves of 1:1:1 Hg(II)-2-ASA(A)- 2,4-DHP (B)System

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

SPECIES DISTRIBUTION CURVES

Species distribution curves were obtained by plotting % concentration of the species obtained through SCOGS[13], against pH.curves are finally sketched by running the computer program ORIGIN 4.0

Study of Species Distribution Curves:

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

The species distribution curves of Hg (II) - 2-ASA - 2, 4-DHP System are presented in fig. 2. In the species distribution curve following species are identified: Protonated ligand species: H_3A, H_2A, HA, BH, Hydroxo species: $Hg(OH)_2$**,** Binary complex species: Hg A and Hg B **,**Ternary complex species: Hg AB.

From the species distribution curves it is clear that binary complex Hg A exist with maximum concentration ~ 38% at the pH ~ 4.2 while the Hg B complex exist with maximum concentration~ 82% at very initial stage of titration which gradually decreases with increase in pH value. In this system ternary species Hg A B exist as a major species attaining maximum concentration ~ 67.9% at ~ 7.5 pH . In this system H_3A, H_2A, HA, and BH species shows their remarkable presence. Hydroxo species $Hg(OH)_2$ present with good existence.

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

For the present system species distribution curves are shown in fig. 3.

In this system following species are identified Pb^{2+}, H_3A, H_2A, HA, BH PbA, PbB and Pb AB. The binary complex of metal with ligand A (PbA) is exist at ~ 6.0 pH with maximum concentration ~ 18% but binary complex of metal with ligand B (Pb B) exist maximum concentration ~ 92% at very initial state of titration which is gradually decreases as the pH raised. The ternary complex species of metal, ligand A and ligand B shows its remarkable presence at higher pH range~9.8 with the maximum concentration of 83%. In this system H_3A, H_2A, HA and BH are present in remarkable value but hydroxo species are not exist.

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Cd (II)- 2-ASA (A) - 2, 4-DHP (B) Ternary System:

The species distribution curves of Cd AB systems are shown in fig .4 In this system following species are identified: Cd^{2+} H_3A, H_2A, HA, BH, $Cd(OH)_2$ $Cd(OH)^+$ Cd A, Cd B and Cd AB.

The binary complex Cd A exist at ~ 6.5 pH having maximum concentration ~ 12% while the CdB complex have the maximum concentration ~ 87% at ~ 6.4 pH which gradually decreases. The ternary complex species shows its presence at higher pH range ~9.4 in maximum concentration is ~ 59%. In the present system Cd^{2+} H_3A, H_2A, HA, BH, Cd $(OH)_2$ and $Cd(OH)^+$ species shows their remarkable presence. HA species exist at ~ 5.6 pH with the maximum concentration ~ 84% which shows decline trend with increase the pH value. Free metal ion concentration is ~79% at start of titration which is gradually decreases as the pH value increases.

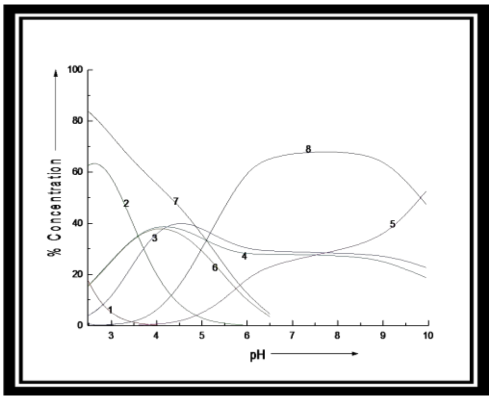

Fig .2-Distribution Curves of 1:1:1 Hg (II)-2-ASA (A) - 2,4-DHP(B) System
(1) H_3A (2) H_2A (3) HA (4) BH (5)$Hg(OH)_2$ (6)Hg A (7) HgB (8)Hg AB
(2)

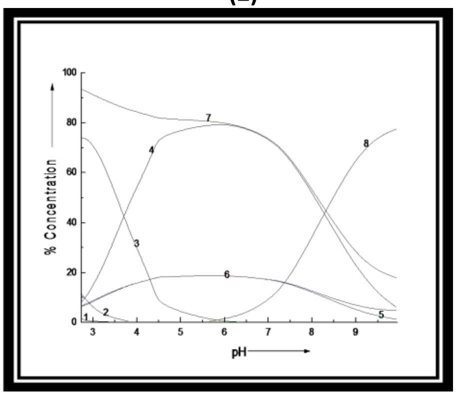

Fig 3- Distribution Curves of 1:1:1 Pb (II)-2-ASA (A) - 2,4-DHP (B)System
(1) Pb^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6)Pb A (7)PbB (8) PbAB

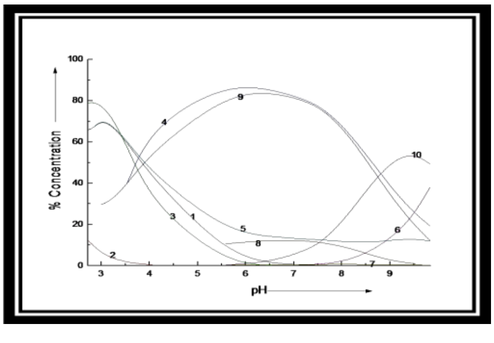

Fig.4.-Distribution Curves of 1:1:1 Cd (II)-2-6ASA (A) - 2,4-DHP(B) System
(1) Cd^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6) $Cd(OH)_2$ (7)$Cd(OH)^+$ (8)Cd A (9)Cd B (10) Cd AB

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The overall stability constants (β_{pqrst}) of binary and ternary complexes are expressed by the general equation in aqueous solutions as follows:

$$pM_1 + qM_2 + rA + sB + t\,(OH) \rightleftharpoons (M_1)_p (M_2)_q (A)_r (B)_s (OH)_t$$

$$\beta_{pqrst} = \frac{[(M_1)_p (M_2)_q (A)_r (B)_s (OH)_t]}{[M_1]^p [M_2]^q [A]^r [B]^s [OH]^t}$$

where the stoichiometric numbers p, q, r and s are either the zero or positive integer and t is a negative integer for a protonated species, positive integer for a hydroxo or a deprotonated species and zero for a neutral species.

Species formed have been considered to exist in the equilibria.

Binary system;

$$M^{2+} + H_2A \rightleftharpoons [MA] + 2H^+$$
$$M^{2+} + BH^- \rightleftharpoons [MB] + H^+$$

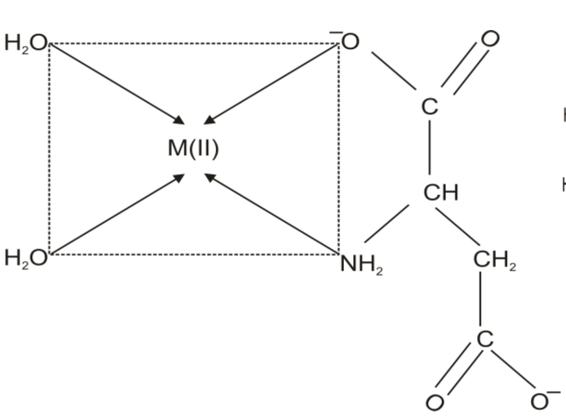
Ternary system;

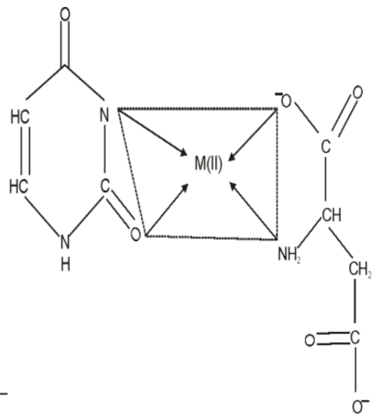
$$MA + BH^- \rightleftharpoons [MAB] + H^+$$
$$M^{2+} + H_2A + BH^- \rightleftharpoons [MAB] + 3H^+$$

General hydrolytic equilibria:

$$M^{2+} + H_2O \rightleftharpoons M_2(OH)^+ + H^+$$
$$M^{2+} + 2H_2O \rightleftharpoons M_2(OH)_2 + 2H^+$$

PROPOSED BINARY AND TERNARY STRUCTURE:





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

Proton-ligand formation constant (log β_{00r0t}/ log β_{000st}) of 2-ASA - 2,4-DHP 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	9.49

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

Complex	Hg	Cd	Pb
$M(OH)^+$	-3.84	-6.89	-9.84
$M(OH)_2$	-6.38	-14.35	-15.54

Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System(1:1)

Complex	Hg	Cd	Pb
MA	13.09	4.39	11.61
MB	13.08	11.45	12.77

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

Complex	Hg	Cd	Pb
MAB	21.00	14.15	18.08

CONCLUSIONS

The stability of all the analogous complexes was in order of Hg (II) > Pb (II) > Cd (II) as anticipated from the increasing charge density along the toxic metal . In term of complex species, the order was ternary >binary, which can be explained based on the increased number of fused rings and the extra stabilization caused by ligand-ligand interactions.

Overall stability order of investigated complexes:

Binary (1:1):

- M (II)-2-ASA (A)

Hg A > Pb A > Cd A

- M (II)-2, 4-DHP (B)

Hg B > Pb B > Cd B

Mixed ligand ternary (1: 1: 1) System

- M (II)-2-ASA (A) - 2, 4-DHP (B)
  Hg A B > Pb A B > Cd A B

REFERENCES

[1] Morgan G.T. and Drew H.D.K. J. Cham. Soc. Trans: (1920) 117,1456 .
[2] Muralidhar Reddy P, Prasad A.V.S.S and Ravinder V., Transition Met. Chem.(2007) **32**. 507.
[3] Muralidhar Reddy P., Prasd A.V.S.S., Shanker K. and Ravider V., Spectrochim. Acta(A). 2007
[4] Okawa H, Furutachi H and Fenton D.E, Coord. Chem. Rew. **174**, 51(1998).
[5] Alexander V. Chem. Rev. (1995) **95**, 273,
[6] Sigel A. and Sigel H.; “Metal ions in Biological System,” Marcel Dekker, New York, (1971-2009) 1-44 .
[7] Yang X.J. and Pin C.; Analyst, (2000) 3, 453
[8] George. St. George, Chem-Chou Chiang and David A. Wilson; Ind.Eng. Chem. Res. (2008) 47 (4), 1277.
[9] Raymond Eller Krik and D. Frederic; ‘Krik-othmer Encyclopedia of Chemical Technology’, John Wiley & Sons Inc., Hooken, Newjersy,(2007) 26, 334
[10] John R. J. Sorenson; Current medicinal chemistry, (2002) 9, 639.
[11] A ntimo D ‘Aniello.Aspartic acid: An endogenous amino acid with animportant neuroendocrine role. Brain Research Reviews (2008) 53:215-214

[12] Welcher F.J., The analytical uses of ethylene diamante tetraacetic acid, D.Van Nostarand Company, New York P. (1957)169.
[13] Sayce I.G., Talanta, (1968)15, 1397.