"IMPACT AND CHEMICAL SPECIATION OF VARIOUS CHELATE COMPOUNDS"

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Abstract: Chelate compounds are very important for all the living being having great impact in the various field of their life and the chemical speciation of these compounds can be studied and analyzed by some advanced analytical methods.

Keywords: Chelate compound, chemical speciation ,SCOGS .species distribution curves etc.

.**Introduction:** The compound which are formed by interaction of single metal ion and ligands having two or more donor atom performing binding action to each other at the result of which a heterocyclic ring structure is formed is named as chelate compound showing the great significance in biological[1]analytical[2] industrial[3,4,] medicinal[5]and other field of life and the various chemical species of binary and ternary chelates with different ratios were studied in this paper.

MATERIALS USED ANDPREPARATION OF SOLUTIONS FOR STUDY:

A 0.01 M sodium nitratesolution of sodium nitrate was prepared whichis essential to maintain the ionic strength and stock solutions (0.01M) of 2- aminosuccinic acid (2-ASA), 2-amino-3-(4-hydroxyphenyl) propanoic acid (2-AHPPA) and 5-methyluracil(5-MU)ligands were prepared and had been standardized against a standard oxalic acid solution while the lead nitrate$Pb(NO_3)_2$ solution was prepared and standardized by EDTA titrations[6] and a carbonate free sodium hydroxide solution used for the present study.

SOLUTIONS

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-ASA (A)* (0.01M) + H_2O

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

Ligand (B) solution: III- 5mL $NaNO_3$ (1.0M) + 5mL HNO_3 (0.02M) + 5mL 5-MU (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 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 Pb (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 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 Pb (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) + ***10 mL 2-ASA (A)*** (0.01M) + 5mL Pb (II) (0.01M) + 10 mL 5-MU (B) (0.01M) + H_2O

RESULTS AND DISCUSSION

The studies 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 chemical speciation of various chelate formed were given by speciation curves which were sketched by using computer program named as ORIGIN 6.0.and the SCOGS[10-12]computer programme was used for the binding constant of investigated chelate compounds.

Table 1

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

Volume of NaOH (mL)	pH			
	A	B	C	D
0.0	2.52	2.74	2.61	3.18
0.2	2.62	2.86	2.84	3.29
0.4	2.73	3.04	3.12	3.54
0.6	2.87	3.37	3.37	4.10
0.8	3.11	5.84	3.54	4.67
1.0	3.65	8.68	3.89	5.02
1.2	9.70	9.20	4.14	5.92

1.4	10.29	9.61	4.36	6.42
1.6	10.53	9.95	4.53	7.03
1.8	10.68	10.20	5.02	7.36
2.0	10.79	10.39	5.29	7.82
2.2	10.88	10.54	5.49	8.26
2.4	10.95	10.66	6.37	8.87
2.6	11.00	10.75	7.04	9.23
2.8	11.05	10.83	7.68	9.67
3.0	11.10	10.89	8.12	10.33
3.2	11.14	10.95	8.49	10.45
3.4		10.99	9.25	10.54

Table -2

Pb (II)- 2-ASA (A) - 5-MU (B) (1:2:2) Ternary System

Volume of NaOH (mL)	pH			
	A	B	C	D
0.0	2.52	2.61	2.41	3.09
0.2	2.62	2.72	2.65	3.18
0.4	2.73	2.85	2.70	3.29
0.6	2.87	3.02	3.75	3.42
0.8	3.11	3.26	3.86	3.57
1.0	3.65	3.60	4.93	3.74

1.2	9.70	4.20	5.12	3.95
1.4	10.29	8.54	6.31	4.19
1.6	10.53	9.40	7.56	4.51
1.8	10.68	9.89	8.74	5.13
2.0	10.79	10.24	9.08	6.17
2.2	10.88	10.47	9.38	6.84
2.4	10.95	10.63	10.21	7.64
2.6	11.00	10.74	10.32	8.68
2.8	11.05	10.83	10.63	9.11
3.0	11.10	10.91	10.74	9.36
3.2	11.14	10.97	10.86	9.55
3.4				9.67

Speciation curves of Pb (II)- 2-AHPPA (A)- 5-MU (B) (1:1:1:) Ternary System

For the present system species distribution curve are represented in fig. 1 and in this system speciation curves reveal the existence of protonated ligand species H_3A, H_2A, HA and B H, free metal ion, binary Pb A, PbB and ternary complex species Pb AB in the variable concentration profile. The ternary complex shows highest concentration ~ 59% at the pH ~ 9.3 binary complex of Pb B shows its maximum concentration ~ 97% at pH ~ 6.0 while the binary complex of Pb A shows maximum concentration ~ 5.8 at the pH~9.0.

Speciation curve of Pb (II)- 2-ASA and 5-M U (1:2:2) Ternary System

The speciation curve for this system is given in fig.-2 and protonated ligand species H_3A, H_2A, HA and BH, free metal ion species: Pb^{2+} (aq.),. binary species Pb A, Pb B and Pb AB ternary species were identified. In this system binary complex of metal and ligand A shows its maximum concentration ~ 12% at pH ~ 4.2. Another binary complex Pb B shows its maximum concentration ~ 92% at start of the titration shows decline trend with raise in pH. H_2A shows the maximum concentration~ 62% at start of the titration while H A existed with the maximum concentration ~ 71%. at ~ 4.3pH. In this system ternary complex of Pb AB is major complex having concentration ~ 98.3% at higher pH ~ 9.5

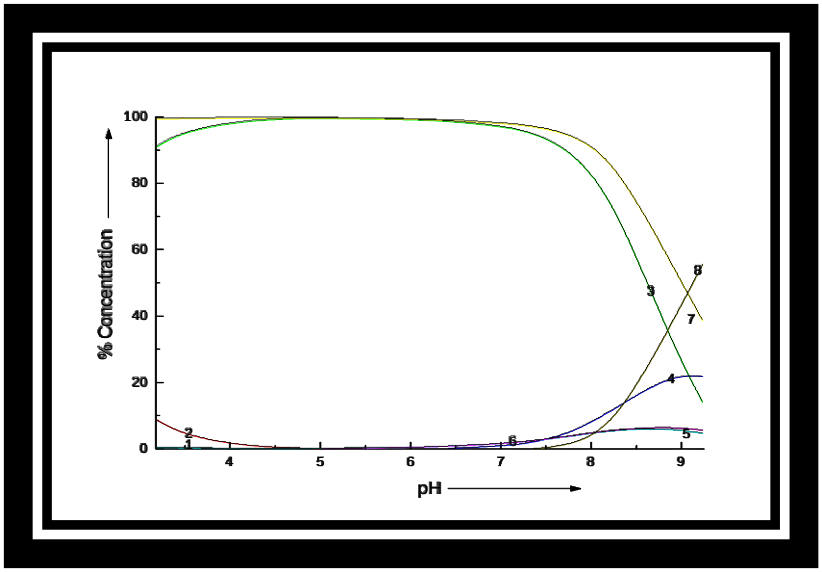


Fig 1-Speciation Curves of (1:1:1) Pb (II)-2-AHPPA (A) - 5-MU (B)System
(1) Pb^{2+} (2) H_3A (3) H_2A (4) HA (5) BH (6) Pb A (7)PbB (8) PbAB

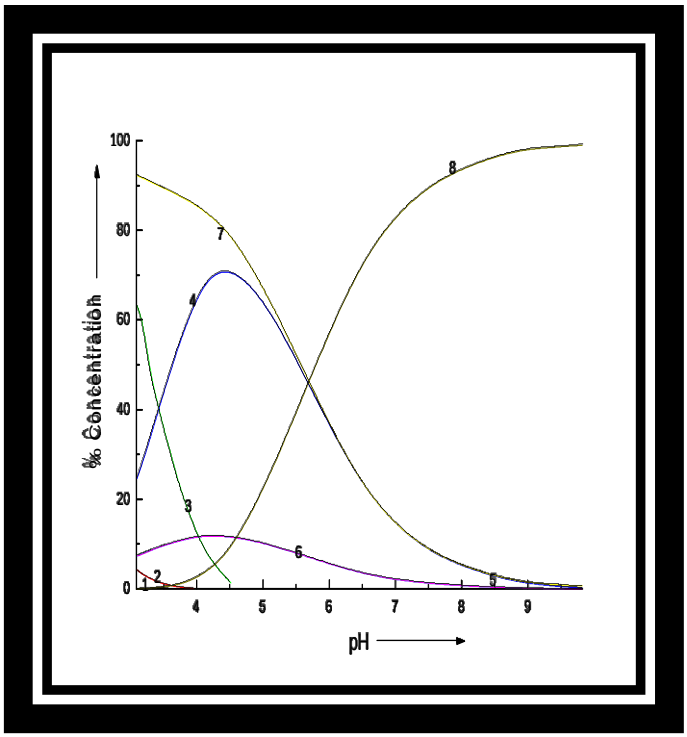


Fig 2-Speciation Curvesof 1:2:2 Pb (II)-2-ASA (A) - 5-MU (B) System

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

Chemical Speciation and Equilibria of Investigated Chelate Compounds:

Formation of Binary Chelate Compound

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

Pb^{++}+ 5-MU(BH^-) [Pb-5-MU] + H^+

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

Formation of Ternary Chelate Compound

[Pb-2-ASA] + BH^- [Pb-2-ASA-5-MU] + H^+

Pb^{++}+ 2-ASA (H_2A) + 5-MU(BH^-) [Pb-2-ASA –5-MU] + $3H^+$

[Pb-2-AHPPA] + BH^- [Pb-2-AHPPA-5-MU] + H^+

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

General hydrolytic equilibria are as follow:

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

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

Calculation of overall stability constant:

The equation for overall stability constants or log ß value ($ß_{prst}$) of the Pb – 2-AHPPA -5-MU (1:1:1) ternary species given as:

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

$[(Pb^{++})_p (2\text{-AHPPA})_r (5MU_s (OH)_t]$

$$\beta_{prst} = \frac{[(Pb^{++})_p (2\text{-AHPPA})_r (5MU_s (OH)_t]}{[Pb^{++})]^p [2\text{-AHPPA}]^r [5\text{-MU}]^s [OH]^t}$$

The overall stability constants or log ß value ($ß_{prst}$) of thePb– 2-ASA -5-MU (1:2:2) ternary species given as:

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

$[Pb^{++})_p (2\text{-ASA})_r (5\text{-MU})_s (OH)_t]$

$$\beta_{prst} = \frac{[Pb^{++})_p (2\text{-ASA})_r (5\text{-MU})_s (OH)_t]}{[Pb^{++})]^p [2\text{-ASA}]^r [5\text{-MU}]^s [OH]^t}$$

β = Overall stability constant, p= M_1,

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

Values of Various Species Investigated in Pb(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 $\pm 1^0$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	9.94

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

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	4.14
MB	13.33

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

Complex	Pb
MAB	17.05]

Values of various species investigated in Pb (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 $\pm 1^0$C, I = 0.1 $NaNO_3$

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

- 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

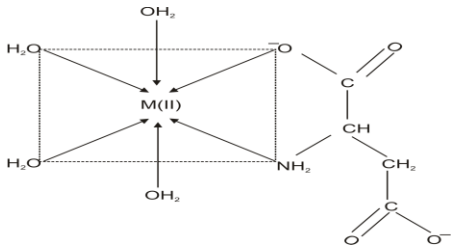
Complex	Pb
MA	11.61
MB	13.33

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

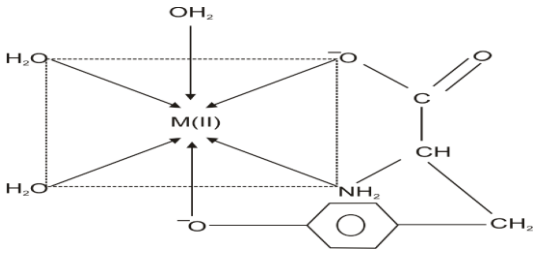
Complex	Pb

MAB	20.54

Proposed Binary Structure;-

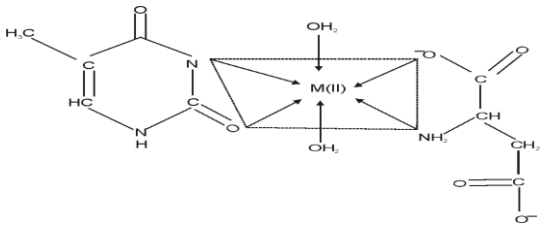


Pb(II)-ASA **6- Coordinated**

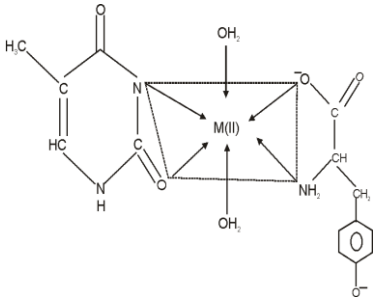


Pb (II)-AHPPA **6- Coordinated**

Proposed Ternary Structure;



Pb (II)-2-ASA-5-MU 6- Coordinated



Pb (II)-AHPPA-5-MU 6- Coordinated

CONCLUSION:

As we discuss above the chelate compound have great impact on our life. In medical field they are use as contrast agents in MRI scanning, chelation therapy, in agricultural the chelation process helps in the removal of heavymetal which is perform by plants, here we studied various binary and ternary chelate compound of Pb with three different chelating ligands with 1:1:1 and 1:2:2 ratioswhich is a valuable method for the reduction of highly toxic effect of lead metal through mixed chelation.

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