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EVALUATION OF BINDING CONSTANT AND IMORTANCE OF VARIOUS BINARY, TERNARY AND QUATERNARY METAL –LIGAND COMPLEXES

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ABSTRACT

The binding constant is a very important factor of coordination complexes which play a very significant role in all the area of our life. Here we discuss about very effective evaluation method using potentiometric analytical technique and SCOGS and ORIGIN computational study applying on Cd (II) and Pb (II) divalent metal ions with 2- ASA and 2,4- DHP as ligand resulting the exact value of binding constants of all the complexes and other species formed in our experiment.

KEYWORDS: *Complexes, Metal Chelates, Binding Constant, ORIGIN, SCOGS*

INTRODUCTION

Complexes of amino acid and nucleobases with metal ions have the very valuable and effective importance in the field of the chemist as well as the medical field. Metal ligand complexes are very useful in the treatment of various types of dangerous diseases like cancer. A complex of technetium-99m with diethylenetriaminepentacetate used in renography which is a form of kidney imaging that uses radiolabelling. Mercapto acetyl tri glycine is a compound that is chelated with radioactive element technetium-99m. Like these most of the drugs act on the basis of chelation. In the field of coordination chemistry, some good and valuable studied were completed by workers[1-6] of various institutes. Present work is a study which is based on chelation and provides very easy and inexpensive method for removal of metal toxicity from the system taking bivalent toxic metal ion Cd (II) and Pb (II) with 2- aminosuccinic acid (2-ASA) as primary ligand (A) and 2,4 dihydroypyrimidine (2,4-DHP) as secondary ligand (B) forming metal –ligand ternary complexes in 1:1:1 ratio and mixed metal mixed ligand quaternary complexes in 1:1:1:1 ratio using potentiometric technique of analysis followed by very advanced computer program SCOGS while graphical representation of various binary, ternary and quaternary complexes is by using another advanced computer program ORIGIN.

MATERIALS AND EXPERIMENTAL PROCEDURES

For the study of metal ligand complexes, metal nitrate solutions have been taken which is standardized by EDTA titrations[7] while binary complexes of Pb (II)/ Cd(II) with primary ligand 2-ASA, Pb(II)/ Cd (II) with secondary ligand 2,4-DHP and ternary complexes of Pb (II)/ Cd (II) with primary ligand 2-ASA and secondary ligand 2,4-DHP in the ratio 1:1:1 and quaternary complex Cd (II)- Pb(II)- 2-ASA-2,4-DHP1:1:1:1 ratio were studied by preparing solution in the way given as under. An electric digital pH meter (Eutech 501) having a reproducibility of ±0.01 with a glass electrode used for potentiometric titration of binary and ternary complexes with the help of Bjerrum's[8]method modified by

Irving &Rossoti Technique[9-10]. The pH meter was calibrated with buffer solutions of pH (4.0) and pH (9.2). All the experiments were completed at a constant temperature of 37 $\pm$ 1^0C using an ultra-thermostat type U_{10} (VEB MLW Sitz, Freital, Germany).

Solutions for Various Investigations

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-ASA (A) (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-ASA (A) (0.01M) + 5mL Cd/ Pb (II) (0.01M) + H_2O

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

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

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

RESULTS AND DISCUSSIONS

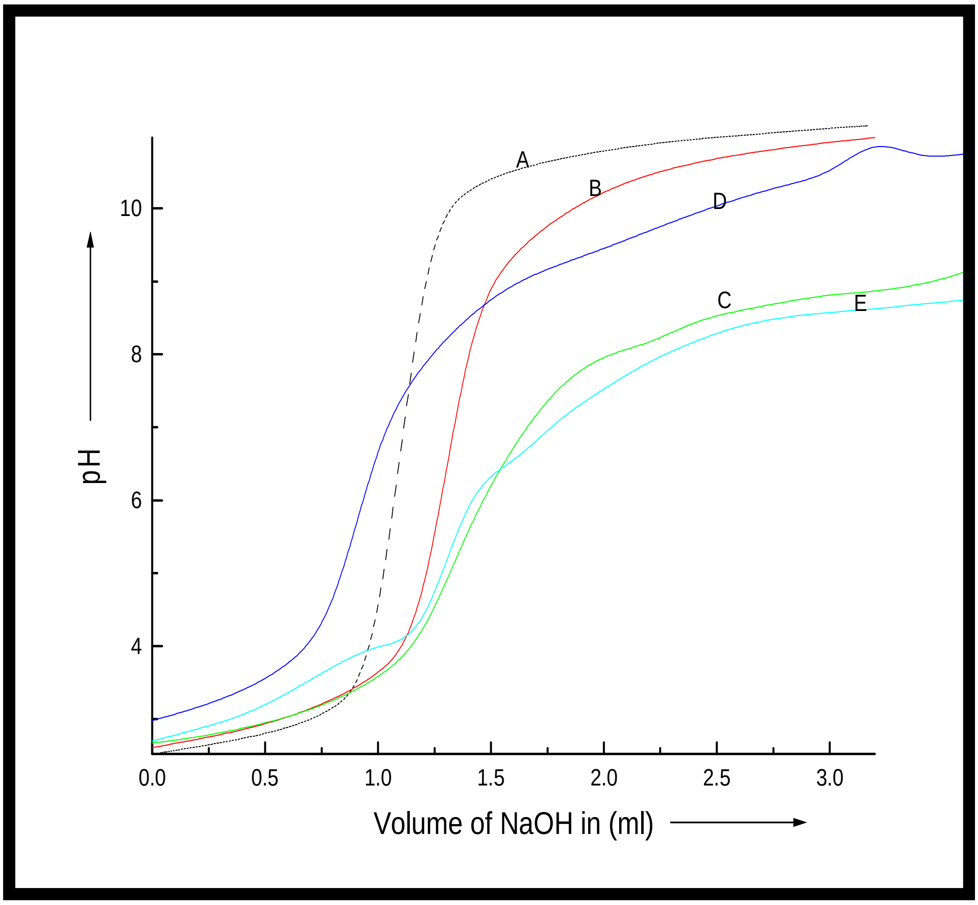
In the present paper a study of metal –ligand interaction were discussed with the help of advanced computer program SCOGS[11-13] (Stability constant of generalized species) as applied in our research papers[14-22]calculating the binding constant while the titration and species distribution curves were sketched by using another advanced computer program named as ORIGIN 6.0. Titration curves were plotted by taking the pH value of acid, ligand, binary and ternary complexes vs. volume of NaOH and species distribution curves was plotted by taking percent (%) concentration of the species against pH.

Table 1: Cd (II)-Pb (II)- 2-ASA (A) - 2,4 –DHP (B) system

Volume of NaOH (mL)	pH				
	A	B	C	D	E
0.0	2.52	2.61	2.67	2.72	2.78
0.2	2.62	2.72	2.75	2.84	2.94
0.4	2.73	2.85	2.87	3.00	3.12
0.6	2.87	3.02	3.02	3.22	3.42
0.8	3.11	3.26	3.24	3.54	3.87
1.0	3.65	3.60	3.55	4.07	4.51
1.2	9.70	4.20	4.07	5.59	6.36
1.4	10.29	8.54	5.66	6.56	6.98
1.6	10.53	9.40	6.77	7.30	7.43
1.8	10.68	9.89	7.59	7.58	7.81
2.0	10.79	10.24	8.00	7.83	8.10
2.2	10.88	10.47	8.14	8.15	8.41
2.4	10.95	10.63	8.46	8.49	8.60
2.6	11.00	10.74	8.60	8.86	8.71

Table 1: Contd.,

2.8	11.05	10.83	8.72	9.22	8.79
3.0	11.10	10.91	8.82	9.55	8.84
3.2	11.14	10.97	8.86	9.84	8.91
3.4			8.95	10.08	
3.6			9.11	10.29	
3.8			9.41	10.48	
4.0			9.82	10.60	
4.2			10.14	10.70	
4.4			10.35	10.77	
4.6			10.51	10.84	
4.8			10.62	10.90	
5.0			10.72	10.95	
5.2			10.79	10.99	



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

Figure 1: Titration Curves of 1:1:1:1 Cd(II)–Pb(II)-2-ASA(A) - 2,4-DHP (B) System

Cd (II) – Pb (II) -2 -ASA (A) - 2, 4 – DHP (B)

The species distribution diagram for this system is given in the fig. 2.In the species distribution diagram following species is identified:

Cd^{2+}, Pb^{2+}, H_3A, H_2A, HA, $Cd(OH)_2$, $Cd(OH)^+$, $Pb(OH)_2$,Pb A, Pb B, Cd AB, Pb AB and Cd Pb AB.

From the distribution diagram, it is evident that the protonated ligand species H_3A, H_2A, and HA have existed in this system. H_3A existed with very low value, but H_2A exists with a higher value having maximum concentration ~72% at the very start of the titration showing a gradual decline trend with the rise in pH. HA first increases till ~ 3.8 pH then starts gradual decrease. Free metal ion Cd^{2+} (aq.) have the maximum concentration ~89 % at the start of titration shows decline trend with an increase in pH, while free metal ion Pb^{2+} (aq.) have lower existence.The binary complex of Cd with ligand A and other binary complex Cd B were observed in a negligible amount in this system. The Pb B complex has maximum concentration ~85% at the start of titration shows decline trend with an increase in pH while the Pb A complex present with lower existence.The ternary complex of Cd AB existed with low amount having maximum concentration ~2.5% at the ~ 6.2 pH value and a ternary complex of Pb AB existed with maximum concentration ~9.0% at the ~8.6pH. Aquaternary complex of Cd PbAB attains the maximum concentration ~88% at the ~ 8.0 pH. Metal hydroxo complexes viz. $Cd(OH)_2$, Cd $(OH)^+$ $Pb(OH)_2$ are observed in this system.Formation of complex species may be attributed to the fall in the protonated ligand as well as free metal ion

Equilibria of Complex Formation

Formation of Binary Complexes

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

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

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

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

Ternary Complex Formed through Two Ways

$$[Cd\text{-}2\text{-ASA}] + BH^- \rightleftharpoons [Cd\text{-}2\text{-ASA-}2,4\text{-DHP}] + H^+$$

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

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

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

Quaternary Complex Formed through Two Ways

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

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

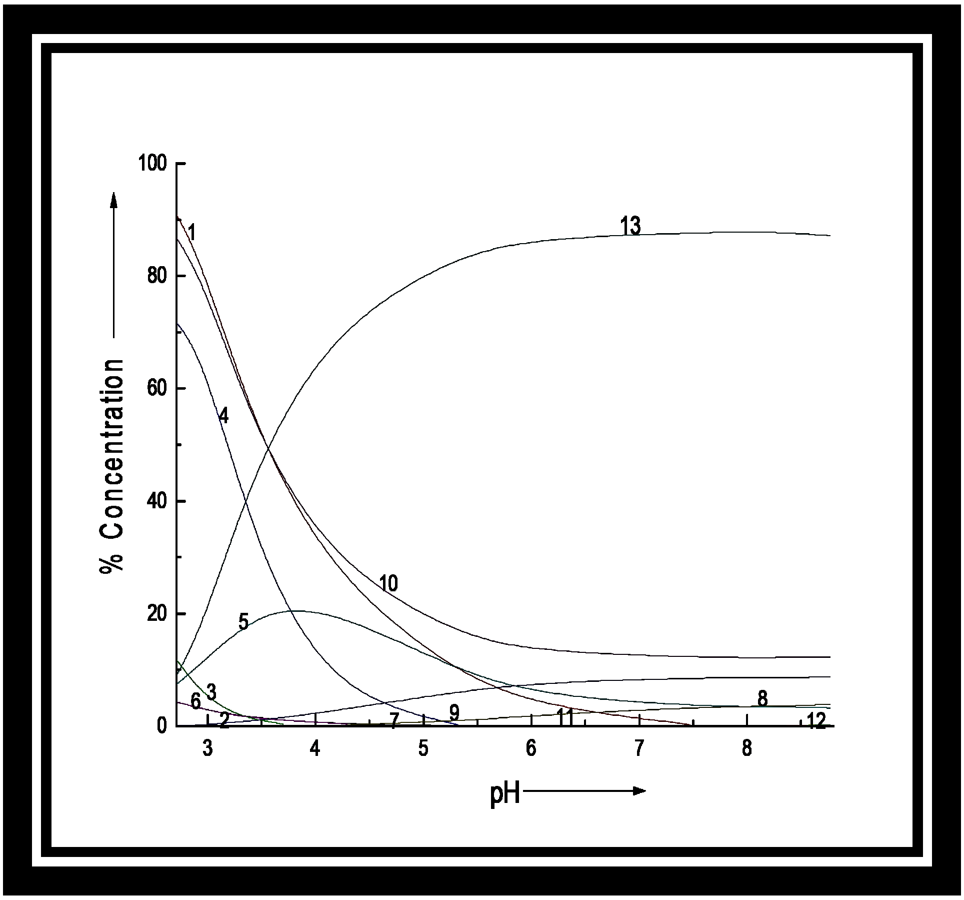
General Hydrolytic Equilibria are as Follow

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

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

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

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



(1) Cd^{2+}(II) (2) Pb^{2+}(II) (3) H_3A (4) H_2A (5) HA (6) $Cd(OH)_2$(7)$Cd(OH)^+$
(8) $Pb(OH)_2$(9)PbA(10)Pb B(11)Cd AB (12) Pb A B(13)Cd Pb AB

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

Evaluation of Binding Constant

The equation for binding or stability constants or log ß value ($ß_{p/qrst}$) of the Cd /Pb – 2-ASA -2,4-DHP ternary species given as:

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

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

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

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

The binding or stability constants or log ß value ($ß_{p/qrst}$) of the investigated Cd-Pb- 2-ASA -2,4-DHP quaternary species was calculated through the equation given as:

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

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

Here β represents binding or stability constant and the stoichiometric numbers p for M_1, q for M_2, r for the primary ligand and s for the secondary ligand while t for the hydroxo species. The value for p, q, r and s either zero or positive integer,t is a negative integer for protonated species, positive for hydroxo or a deprotonated species and zero for neutral species.

Propesed Binary, Ternay and Quaternary Complex Structures

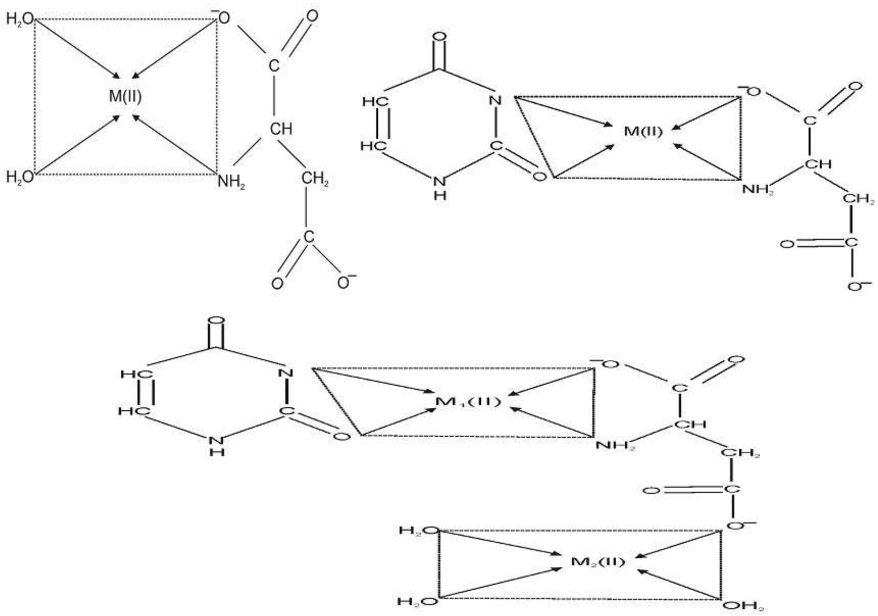


Figure 3

Binding Constants and Other Related Constants of Binary, Ternary and Quaternary Complexes for M_1(II)- M_2(II) 2-ASA(A)-2,4-DHP(B) System

Table 2: Proton-Ligand Formation Constant ($\log\beta_{00r0t}$/ $\log\beta_{000st}$) of 2-ASA- 2,4-DHP at 37 ± 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	9.49

Table 3: Hydrolytic Constants of M^{2+} (aq.) Ions. ($\log \beta_{p000t}$/ $\log \beta_{0q00t}$)

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

Table 4: Metal-Ligand constants (log β_{p0r00}/ log β_{0qr00}/ log β_{po0s0}/ log β_{0q0s0}) Binary System

Complex	Cd	Pb
MA	4.39	11.61
MB	11.45	12.77

Table 5: Metal-Ligand Constants (logβ_{p0rs0}/ logβ_{0qrs0}): Ternary System (1:1:1)

Complex	Cd	Pb
MAB	14.15	18.08

Table 6: Metal-Ligand Constants (Log $\beta_{pqrst)}$: Quaternary (1:1:1:1) System

Complex	Cd-Pb
M_1 -M_2-A-B	27.72

CONCLUSIONS

The present study is a qualitative attempt to evaluate binding constant which is essential for understanding the various vexed problem of pharmaceutical, biological, analytical chemistry because the metal-ligand interaction depends upon the relative and absolute concentration of all the kind of ligand present as well as on the relevant pK, binding constant and pH of the solutions.

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