



METAL – LIGAND EQUILIBRIA IN SOLUTION PHASE A POTENTIOMETRIC STUDY

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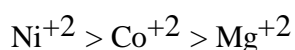
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ABSTRACT

pH – metry investigation on the complex formation equilibrium of Ni²⁺ (M₁), Co²⁺ (M₂) and Mg²⁺ (M₃) with Glycine (Gly) (L₁) as a primary ligand and p- amino benzoic acid (p-ABA) (L₂) or p-hydroxy benzoic acid (p-HBA) (L₃) as a secondary ligand shows the formation of ternary systems. For present work different molar ratios of the metal, primary ligands and secondary ligands 1:5:5 & 2:3:3 are used. The ionic strength of 0.1 Molar was kept constant using NaNO₃. The glycine and p-ABA or p-HBA with metal shows stability constant in order of



Keywords: Potentiometric Studies, Ternary Complexes, Glycine, p- amino benzoic acid, p-hydroxy benzoic acid, Mixed-Ligand Complexes, Stability constant

INTRODUCTION.

In continuation of our previous work¹⁻⁴ We decided to study complexation in different metal to ligand ratios. 1:5:5 & 2:3:3. Glycine (L₁) is a α -amino acid and building block of protein. Its



interaction with metals and other molecules will lead to understand various biological processes. Literature survey reveals that very less work has been done on the study of stability constant of ternary complexes (M:L₁:L₂) by using molar ratios 1:5:5 & 2:3:3. The stability constant value of this ternary complexes in different metal to ligand ratios helps us to understand the interaction between metal – primary ligand and secondary ligand. To understand this interaction becomes the bases for this potentiometric study. Almost no work has been done in these molar ratios using Glycine (L₁) as a primary ligand and p-amino benzoic acid (L₂) and p-hydroxy benzoic acid (L₃) as a secondary ligand therefore we decided to undertake present investigation.

EXPERIMENTAL

All chemicals used in this study were of A.R. grade obtained from S D. fine chemicals Ltd. Double distilled water was used for preparation of solutions. The NaOH solution of requisite concentration was prepared and standardized by using potassium hydrogen phthalate. The ionic strength in all setup was maintained by using NaNO₃ solutions. The entire experimental set up is as follows.

Set – I HNO₃ (0.1 M) + NaNO₃ (1 M)

Set – II HNO₃ (0.1 M) + NaNO₃ (1 M) + Glycine (L₁) (0.1 M)

Set - III HNO₃ (0.1 M) + NaNO₃ (1 M) + Glycine (L₁) (0.1 M) + Metal (0.1 M)



- Set – IV HNO_3 (0.1 M) + NaNO_3 (1 M) + p-ABA (L_2) or p-HBA (L_3) (0.1 M)
- Set – V HNO_3 (0.1 M) + NaNO_3 (1 M) + p-ABA (L_2) or p-HBA (L_3) (0.1 M)
+ Metal (0.1 M)
- Set - VI HNO_3 (0.1 M) + NaNO_3 (1 M)+Glycine (L_1) (0.1 M)+p-ABA (L_2) or
p-HBA (L_3) (0.1M)+Metal (0.1 M)

Each set of solution was diluted to 50 mL in a standard flask. Each solution was titrated separately with standard NaOH solution. A Pre-calibrated pH-meter Elico-L1 120 was used to monitor the pH during titration. The $\log K_{MX}$ and $\log K_{MXY}$ values were calculated by using computer programme in Excel.

RESULTS AND DISCUSSION

For the present work we have taken nitrates of nickel (M_1), cobalt (M_2) and magnesium (M_3). The nickel and cobalt are from transition metal series and well-known for Complexation. Magnesium is also equally important from biologically point of view. The protonation Constants of both secondary ligands in the molar ratio 1:5 & 2: 3 has been determined by the same titration method and are presented in the Table-. The ___ values were also evaluated for the same , comparatively the protonation constant values of p-HBA is more than p-ABA. This may be due to the difference in the substitute group. Since phenolic OH is a acidic group and amino group is basic in nature. The hydroxyl group decrease the protonation constant or basic amino group shows strong affinity for proton and forms a co-ordinate bond. The metal-ligand stability constant



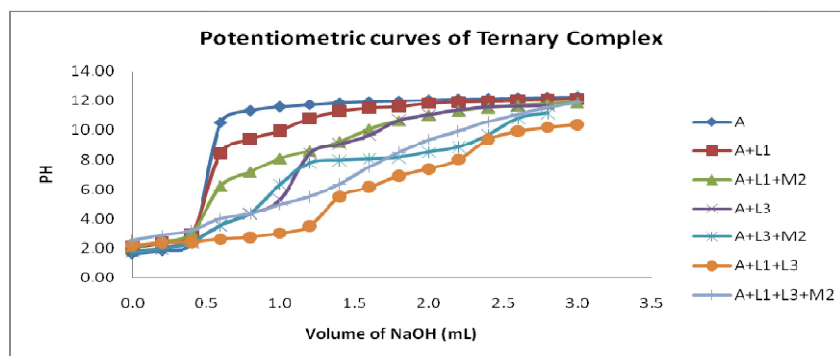
for binary system under 1:5 & 2:3 ratios. Were also calculated using point- wise method. These are represented in Table-2. There is no regular trends in the stability constant values, we were unable to get stability constant for Ni - Gly (2:3), Ni - p - ABA (1:5), Co - p-ABA (2:3) and Mg - p-ABA (2:3). In the titration curves for the system a single inflection point was observed for ternary complexation which indicate that simultaneous equilibria exist instead of stepwise addition of ligand to the metals⁵. i.e.



The $\log K_1^H$ evaluated for the ligands p-ABA (L_2) and p-HBA (L_3) are given in the following. From the ligand and metal titration curves the values of \bar{n} and from that values of P^L were obtained. The variation in \bar{n} was found to be 0 to 2 which indicate that the complexation

Table 1- Protonation constant of ligand

Ligands	$\log K_1^H$	$\log K_2^H$	$\log \beta^H$
p-ABA (L_2)	04.42501	02.95535	07.38036
p-HBA (L_3)	08.89774	04.12694	13.02468



The log K_{MXY} values for Ternary Complexes of p-ABA (L_2) and p-HBA (L_3) are shown in Table-3.

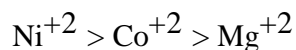
These values are used to calculate

$$\Delta \log K = \log K_{MXY} - (\log K_{MX} + \log K_{MY})$$

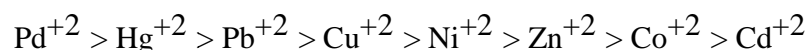
We observed that Mg shows negative to $\Delta \log K$ except for p-ABA (2:3) in Glycine similarly Co & Ni shows all positive $\Delta \log K$ values except at p-HBA (2:3). These exceptions are due to the reasons that we does not get values for corresponding binary complexes. The behavior of Mg is exactly opposite to Co & Ni, because Mg belong to alkaline earth metal group i.e. s block element and Co & Ni belongs to transition metals i.e. d block elements .

The transition metal make available there d orbitals to form a stable complex. There fore stability constant values for transition elements ternary complex is more compare to respective stability constants of binary complexes.

During the present work, we observed that in almost all the cases the stability constant values were in the order of-



The high value of stability constant for Ni^{+2} and Co^{+2} shows that d-block elements forms more stable complexes due to the availability of d-orbitals which is able to accommodate electrons of the ligands. Mg^{+2} although forms complexes but due to unavailability of d-orbitals, It is weaker complex then Ni^{+2} and Co^{+2} metal ions. This is also in accordance with the Monica Saladini and Co-workers ⁶ who reported that stability constant of metals with nitrogen protected amino acid shows the following order of stability,



This indicates that the metal affinity for Ni, oxygen donor ligands is the major factor determining the stability constant. The order for different metal, ternary complexes reported by Eman Shoukry ⁷ is-





Table-2: Metal – Ligand stability constant of Binary complexes by point –wise method

Ligand	Ratio	Metals	Stability Constant
	1:5	Ni	02.56930
		Co	02.97061
		Mg	02.84761
Glycine	2:3	Ni	-
		Co	03.28327
		Mg	02.68657
p- ABA	1:5	Ni	-
		Co	02.84050
		Mg	02.97986
	2:3	Ni	02.65349
		Co	-
		Mg	-
p- HBA	1:5	Ni	03.05396
		Co	02.68644
		Mg	03.08548
	2:3	Ni	02.82179
		Co	02.91900
		Mg	02.85358



Table-3: The log K_{MX_2Y} and $\Delta \log K$ values for Ternary Complexes

M:L1: L2	Metal			$\Delta \log K$	
		p-ABA (L_2)	p-HBA (L_3)	p-ABA (L_2)	p-HBA
1:5: 5	Ni	7.56794	8.08423	04.99864	02.46097
	Co	6.26244	6.22945	0.45133	0.5724
	M	3.86322	4.58159	-1.96425	-1.3515
2:3: 3	Ni	8.37373	8.35563	05.72024	05.53384
	Co	6.39412	6.05987	03.11085	-0.1424
	M	4.50326	4.18138	01.81669	-1.35877

The values of stability constant reveal that- :

1. The formation of ternary complex is confirmed by decrease in pH. This is due to release of H^+ ions from the secondary ligands
2. The mixed-ligand curve lie below the pure ligand as well as those of binary metal ligand curves indicating the formation of $(M:L_1:L_2)$ complex species.
3. The pH of hydrolysis in all the mixed-ligand complexes studied was found to be higher than the pH of hydrolysis of the individual complexes.
4. There was no drift in the pH values due to hydrolysis precipitation upto the pH range studied for respective system.
5. Since the mixed-ligand curve did not coincide with either of the individual metal titration curves in the lower pH range, the formation of complex by simultaneous equilibria was inferred.
6. The formation of mixed complex species in solution was supported by absence of any solid phase during the titration of ternary mixture.

ACKNOWLEDGMENTS

We are thankful to Dr. Maqdoom Farooqui, Principal, Maulana Azad College, Rauza Baugh, Aurangabad, (M.S.) India for providing laboratory facilities.



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