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A POTENTIOMETRIC STUDY OF STABILITY CONSTANT OF TERNARY COMPLEXATION OF SOME METALS

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ABSTRACT

pH – metry investigation on the complex formation equilibrium of Ni^{2+}, Co^{2+} and Mg^{2+} with Glycine (Gly) and p–amino benzoic acid (p-ABA) or p-hydroxy benzoic acid (p-HBA) shows the formation of ternary systems. For present work different molar ratios of the metal, primary ligands and secondary ligands are used. The ionic strength of 0.1 Molar was kept constant using $NaNO_3$. The complex formation equilibrium was elucidated with the help of speciation curves. The glycine and p-ABA or p-HBA with metal shows a order of $Ni^{+2} < Co^{+2} < Mg^{+2}$

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

INTRODUCTION

There are various papers appeared in last few decades regarding ternary complexes of transition and non transition metals.[1-7] Glycine 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 ($M:L_1:L_2$) by using molar ratios 1:1:1, 1:2:2, 1:1:2, 1:2:3. Almost no work has been done in these molar ratios using Glycine as a primary ligand and p- amino benzoic acid and p-hydroxy benzoic acid as a secondary ligand therefore we decided to undertake present investigation.

EXPERIMENTAL

All chemicals used in this study were of Analar 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 pthalate. The ionic strength in all setup was maintained by using $NaNO_3$ solutions. Following sets of solutions were prepared.

1. HNO_3 (0.1 M) + $NaNO_3$ (1 M)
2. HNO_3 (0.1 M) + $NaNO_3$ (1 M) + Glycine (0.1 M)
3. HNO_3 (0.1 M) + $NaNO_3$ (1 M) + Glycine (0.1 M) + Metal (0.1 M)
4. HNO_3 (0.1 M) + $NaNO_3$ (1 M) + p-ABA or p-HBA(0.1 M)
5. HNO_3 (0.1 M) + $NaNO_3$ (1 M) + p-ABA or p-HBA (0.1 M) + Metal (0.1 M)
6. HNO_3 (0.1 M) + $NaNO_3$ (1 M)+Glycine (0.1 M)+p-ABA or p-HBA(0.1 M)+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 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, cobalt and magnesium. The nickel and cobalt are from transition metal series and well-known for Complexation. Magnesium is also equally important from biologcally point of view.

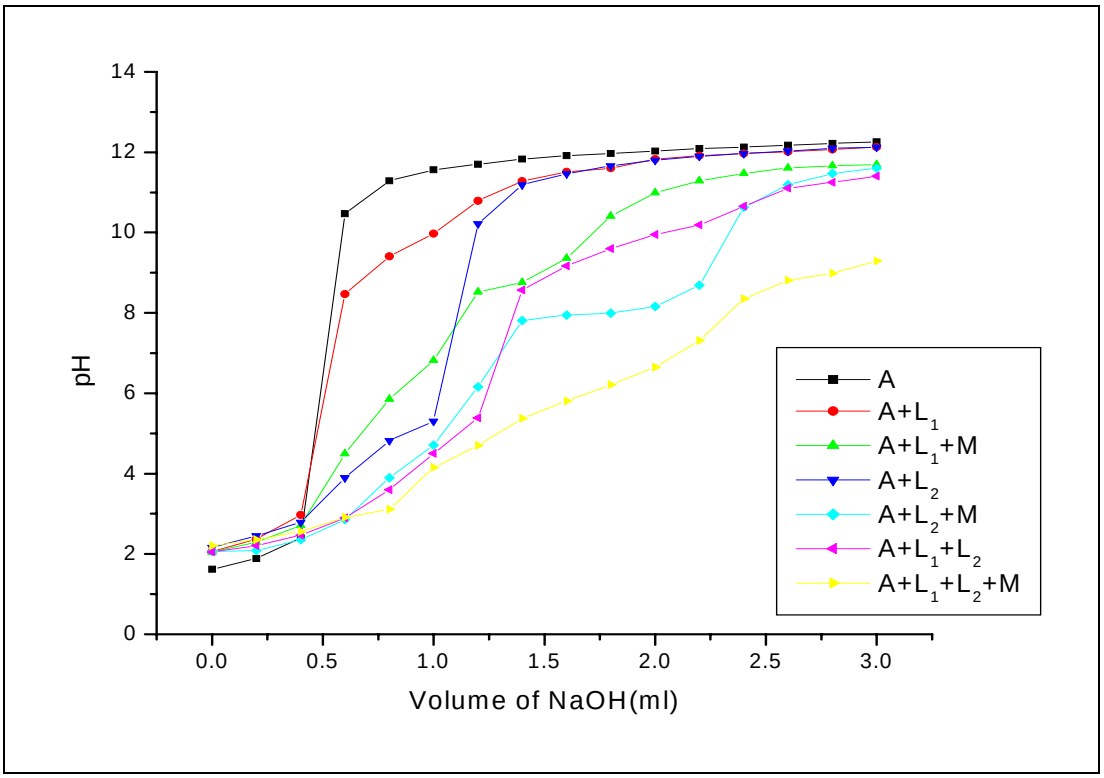

Fig.-1: Titration curves (M= Nickel, L_1= Glycine, L_2= PAB, A= HNO_3)

The values of stability constant reveal that- :

1. A decrease in pH when the secondary ligand (A) is added to the (M:L) solution suggests the release of protons due to ternary complex formation.
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.

The log K_{MXY} values for Ternary Complexes of p-ABA and p-HBA are shown in Table-1.
During the present work, we observed that in almost all the cases the stability constant values were in the order of-

$$Ni^{+2} < Co^{+2} < Mg^{+2}$$

This is in accordance with the Monica Saladini and Co-workers [8] who reported that stability constant of metals with nitrogen protected amino acid shows the following order of stability,

$$Pd^{+2} > Hg^{+2} > Pb^{+2} > Cu^{+2} > Ni^{+2} > Zn^{+2} > Co^{+2} > Cd^{+2}$$

Which 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 [9] is-

$$Ba^{+2} < Sr^{+2} < Mg^{+2} < Mn^{+2} < Cd^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}$$

The order of stability depends on pair of ligands used for Complexation, it was reported that[10] Cu-Hydroxamate complexes do not significantly favor mixed ligand complex formation with amino acids having only the carboxylate and amino groups; however these complexes are strongly formed with study histidine, due to the presence of the imidazole group.

It was reported that[11] the stability of ternary complexes depends on several factors such as a double bond present in a ligand increases stability of the complex due to exocyclic conjugation, the OH group present in the ligand increases stability due to electron withdrawing nature, if the ring form is bigger, the stability will be low. The methylene group is present in the ligand decreases complex tendency of the ligand, if the ligand is trans isomer, stability is less and for six cis-isomer stability is higher. The stabilizing effect of chelation for histamine shows that stability is more compared to imidazole.[12]

The stability constant values for Glycine – p-ABA pair in Ternary Complex shows maximum values at the molar ratio of 1:2:2 for Ni^{2+} and Co^{2+} but in case of Mg maximum values for 1:1:2 for Glycine –p-HBA pair, the maximum stability constant values was observed for 1:1:1 complex of Co^{2+} and Mg^{2+}, where as for Ni^{2+}, maximum values for 1:1:2, these values suggests that if molarity of primary and secondary ligands is same the stability is high.

Table-1: The log K_{MXY} values for Ternary Complexes

$M:L_1:L_2$ Ratio	Metals	Ligands	
		p-ABA	p-HBA
1:1:1	Ni	7.86870	8.26887
	Co	5.88148	6.96344
	Mg	3.79294	4.30083
1:2:2	Ni	8.20314	7.58044
	Co	6.69750	6.12650
	Mg	4.25184	3.90077
1:1:2	Ni	7.76311	8.46480
	Co	5.71325	5.83888
	Mg	4.44638	4.00740
1:2:3	Ni	7.76861	7.56358
	Co	6.29447	6.39581
	Mg	4.41438	3.88321

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Erratum

A typographical error has been published in the research paper entitled, "**Synthesis and antimicrobial…….pyrimidines", RJC, Vol.2, No.1, 167-173 (2009) by Md Salahuddin, Sanjay Singh and S.M.Shantakumar.** The corrections to be done in page No. 170, Para No. 04, under the heading Antimicrobial activity.

Readers, please read the sentence *"Antimicrobial activity was determined by the Disc Diffusion Method."* in place of the sentence *"The minimum Inhibitory concentration (MIC) was determined by the paper Disc Diffusion Method."*Thank You.

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