"STABILITY CONSTANTS DETERMINATION OF DIVALENT METAL IONS IN TERNARY COMPLEXATION : A POTENTIOMETRIC STUDY"

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ABSTRACT

pH – metry investigation on the complex formation equilibrium of Ni^{2+} (M_3), Co^{2+} (M_2) and Mg^{2+} (M_1) with Glycine (Gly) (L_1) as a primary ligand and Oxalic acid (OXA) (L_2) or Malonic acid (MAL) (L_3) as a secondary ligand 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 NaNO3. The glycine (L_1) and OXA (L_2) or MAL (L_3) with metal shows a order of $Ni^{+2} > Co^{+2} > Mg^{+2}$

Keywords: Potentiometric Studies, Ternary Complexes, Glycine, Oxalic acid, Malonic acid, Mixed-Ligand Complexes,Stability constants, Calvin- Bjerrum method.

INTRODUCTION

For the present work we have used glycine (L_1) as a primary ligand and dicarboxylic acids such as oxali and malonic as secondary ligands. There are various papers appeared in the literature regarding complexation of glycin (L_1) alone [1] or glycin along with other ligands [2,3] . Literature survey reveals that there are various ligands used , which gives that there are various ligands used, which gives complexation [4-8] with Ni (M_3), Co (M_2) or Mg (M_1). Glycine (L_1) 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

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(M:L_1:L_2) by using molar ratios 1:5:5, 1:5:6, 2:3:3, 2:3:4. Oxalic acid and Malonic acid are bidentate ligand and there fore able to form more stable complexes as compared to mono-dentate ligands. Almost no work has been done in these molar ratios using Glycine (L_1) as a primary ligand and Oxalic acid (L_2) and Malonic acid (L_3) as a secondary ligand.

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.

Experimental Set	Solutions Prepared
Set – I	HNO_3 (0.1 M) + $NaNO_3$ (1 M)
Set – II	HNO_3 (0.1 M) + $NaNO_3$ (1 M) + Glycine (L_1) (0.1 M)
Set – III	HNO_3 (0.1 M) + $NaNO_3$ (1 M) + Glycine (L_1) (0.1 M) + Metal (0.1 M)
Set – IV	HNO_3 (0.1 M) + $NaNO_3$ (1 M) + OXA (L_2) or MAL (L_3) (0.1 M)
Set – V	HNO_3 (0.1 M) + $NaNO_3$ (1 M) + OXA (L_2) or MAL (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)+OXA (L_2) or MAL (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 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

A Calvin – Bjerrum method was used to find out stability constants of Ni (M_3), Co (M_2) and Mg (M_1) metals with above mentioned ligands. 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 complexation was carried out in presence of $NaNO_3$ to maintain the ionic strength. The pH-metre data was used to calculate $\bar{\eta}_A$, from wich protonation constants were calculated .Further the pH-metric readings were used to calculate $\bar{\eta}$ for ternary complex, from which stability constants were find out.

The values of stability constant reveal that-:

1. The release of H^+ ions from secondary ligands like oxalic acid and malonic acid, lowers the pH value which isalso indication of the formation of ternary complex.

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 [9] of OXA (L_2) and MAL (L_3) 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- $Ni^{+2} > Co^{+2} > Mg^{+2}$

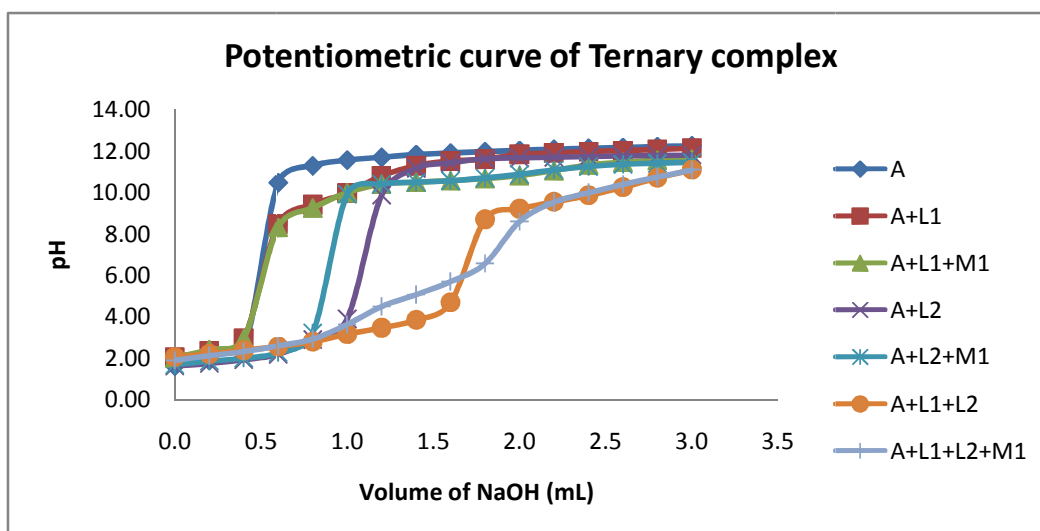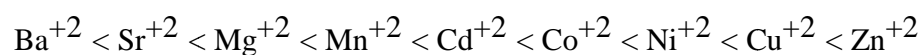The order for different metal, ternary complexes reported by Eman Shoukry [10] is

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

Fig: 1: (M₁ = Magnesium, L₁ = Glycine, L₂ = Oxalic acid, A = HNO₃)
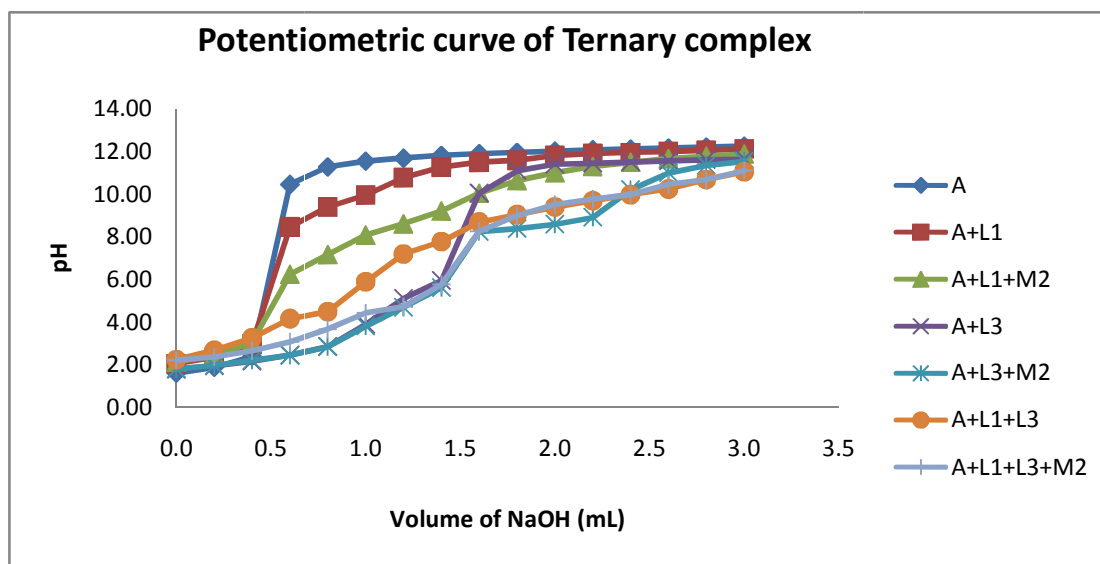
Fig: 2: (M₂ = Cobalt, L₁ = Glycine, L₃ = Malonic acid, A = HNO₃)

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2:3:3 , 1:5:6 and 2:3:4 for Ni^{+2} (M_3) and Co^{+2} (M_2) for both the secondary complexes i.e oxalic acid (L_2) and malonic acid (L_3) are stable. However very low value is obtain in case of 1:5:5 for Ni^{+2} (M_3) and Co^{+2} (M_2) when the secondary ligand is malonic acid indicating that primary complex of glycine (L_1) is quiet stable and malonic acid (L_3) forms complex with difficulty. Mg metal is an s- block element which leacks the presence of d-orbitals and there fore it froms less stable complexes when compared with Ni and Co in all different ratios. As Ni and Co are d-block elements, which are able to from stable complexes. The stability constant value is least for Mg in metal ligand ratio 2:3:3. The order of stability depends on pair of ligands used for Complexation.

The values of $\log K_{MXY}$ for all systems reveals that nickel form most stable complexes over entire range of concentrations of primary ligand and secondary ligand. The magnesium complexes shows low valus for $\log K_{MXY}$ may be due to the fact that it does not possess empty d-orbital, hence a weak Lewis acid. For all ratio and for both ligands the trend remains almost constant , indicating that concentration of ligand has little effect on the complexation compared to the nature of ligand. The values for oxalate complexes is more than malanato complexes which confirm this hypothesis.

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

M:L$_1$:L$_2$ RATIO	METALS	LIGANDS	
		OXALIC ACID (L_2)	MALONIC ACID (L_3)
1:5:5	Ni	7.72782	7.87221
	Co	6.39823	6.28530
	Mg	4.56505	4.42647
2:3:3	Ni	8.44274	8.05018
	Co	6.30180	6.14987
	Mg	3.88159	4.00745

1:5:6	Ni	8.19112	7.67570
	Co	6.24433	6.53336
	Mg	4.86692	3.81745
2:3:4	Ni	8.36148	8.24878
	Co	5.82480	5.95950
	Mg	4.35900	4.47096

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