pH metric Studies on Complexation of 4-Amino Benzoic Acid (PABA) with transition metal ions

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Abstract

The stability constants of metal complexes of PABA with transition metal ions have been evaluated pH metrically in aqueous solution at 27° C temperature and 1N ($NaNO_3$) ionic strength. Protonation constant and formation constant were determined by using Irving Rossoti titration method with SCOGS Computer programme. Metal ligand ratio was 1:2.

Introduction

Some drugs show enhanced activity when administered as metal complexes. To understand the complex formation ability of the ligands and the activity of complexes, it is essential to have the knowledge about solution equilibria involved in the reactions. The extent to which the ligand binds to metal ions is normally expressed terms of stability. A survey of literature reveals that study on complexation of PABA is very scarce, therefore study was undertaken in continuation with our earlier studies.[1]

PABA is a naturally occurring, water soluble compound. It is found in many foods as cofactor of the vitamin B complex. It is a non protein amino acid broadly distributed in the nature. It is intermediate in the synthesis of folic acid in bacteria. Sulfonamide antibiotics are structural similarity with PABA and interfere with the synthesis of nucleic acid in sensitive microorganisms by blocking the conversion of PABA to coenzyme dihydro folic acid. In humans dihydro folic acid is obtained from dietary folic acid. A human lacks the ability to synthesize foltae from PABA. In humans, the concentration of Cadmium in blood serum may be reduced by ligand therapy; therefore the study of cadmium complexes has a great importance.

Experimental

All the chemicals used of high purity. Ligand sample was of SD Fine AR grade. All the solutions were prepared in double distilled water. All the solutions were standardized before use by known methods. Metal nitrates were used due to their high solubility in water. 1N ($NaNO_3$) used for maintaining ionic strength.

Glass electrode with digital potentiometer (ELICO LI-20) was used for pH measurement. pH meter was calibrated using buffer solution of pH = 4 and pH = 7 before titration. The experimental procedure involved three titrations (I) HNO_3 (A) (II) HNO_3 + Ligand (A + L) (III) HNO_3 +Ligand + metal (A + L + M) against 0.2 N NaOH. Proton ligand and metal ligand stability constant were determined by using SCOGS computer programme.The results obtained for each titration was plotted as a volume of NaOH vs. pH and related volume at succeeding pH determined and calculated.

RESULTS AND DISCUSSION

The titration curves were separated from each other each taking approximately S shape. The end point for the titration increased in the order I > II > III. The maximum value of *n* did not exceed two for all complexes indicating the formation of 1:1 and 1:2 complexes.

Considerable separation of metal complexes curve from reagent curve along volume axis is an evidence for complex formation. The use of very dilute solution ruled out the possibility of formation of polynuclear complexes.

Average numbers of protons associated with ligand were calculated from acid and ligand titration curve and used to get pKa values. From table**1** it is clear that PABA has the highest pKa value due to primary amino group ($-NH_2$) group and lower value due to carboxylic group. The pKa values obtained by half integral and point wise method are in agreement. $\overline{n_A}$ Vs. pH plot was obtained between 0-2 indicating that the ligand has two dissociable protons. The maximum value of *n* obtained was 2 indicating the formation of 1:1 and 1:2 complexes.

Table1. Stability constants of 4-aminobenzoic acid (1:2)

pK_H	Metal ion	Log K_1	Log K_2	Log β
a) $pK_1 = 4.6850$	Co (II)	3.2331	3.8327	7.0658
a) $pK_2 = 9.1620$	Cu (II)	3.7159	3.2199	6.9359
	Fe (III)	3.1574	3.1443	6.3017
b) $pK_1 = 4.7760$	Ni (II)	3.0666	3.1184	6.2690
b) $pK_2 = 8.8800$	Zn (II)	3.1246	3.1213	6.2460
	Cd (II)	3.1201	3.1121	6.2323
a = Half integral, b = Point wise				

The pKa values obtained by Half integral and point wise method and found to be in agreement. The carboxylic group is a normally stronger acid than amino group. The results obtained are in agreement with literature cited.

The order of stability constant for the investigation is   Co (II) > Cu (II) > Fe (III) > Ni (II) > Zn (II) > Cd (II). The order indicates that Co and Cu have high affinity for complex formation and Cd has least affinity.

For metal ions of Co and Ni, $logK_2$ are higher than $logK_1$, indicating that vacant sites of these metal ions are easily available for bonding of the first ligand than second one. For rest of the metal ions $logK_1$ are higher than $logK_2$, indicating that the interaction of second ligand is weaker than first. We reported same trend of stability with 2,2bipyridyl [2].

Vighe et al studied the stability constants of Co Prolyl-alanine (PA) complexes; they reported two pKa values as 6.10 and 9.00 for PA [3]. Farooque Ansari studied stabilities of (Mg, Ni, and Co) with PABA by potentiometric methods, he reported pKa value as 5.9153 and high stability values for Ni than rest metals [4]. Pulimadi Reddy et al studied interaction of the amino acids with Cobalt, reported two pKa values for glycine as 2.48 for carboxylic group and 9.53 for amino group [5]. Paula Gamerio et al studied interaction of Fluroquinolones and reported two pKa values for Fluroquinolones , 7.9-8.9 corresponding to basic piperazinyl ring and 5.7-6.2 to carboxylic group in the 3-position. Higher pKa for acid value may be due to intramolecular hydrogen bond between keto group and carboxylic group [6]. Santosh Narayan chadar et al pointed out the possibility of coordination through $-NH_2$ in case of PABA and use of the ligand to reduce the Cadmium toxicity [7].

References

1. Sayyed Hussain, S. A. (2014). Potentiometric studies of P-amino Benzoic Acid with transition metaions. *World Journal of Pharmacy and Pharmaceutical Sciences, 3* (5), 632-635.

2. Shaikh Abdul Rahim, SayyedHussain, MazaharFarooqui.(2015). Studies of binary complexes of metal ions with 2, 2-Bipyridyl by potentiometry, *Chemical Science Transactions, 4(1)*, 176 - 180 DOI : 10. 7598 / cst 2015. 92

3. D.S. Vighe, J. B. (2006). Studies of the effect of ionic strengths on stability constants of Co(II) Prolyl- alanine complexes. *Asian Journal of Chemistry, 18* (4), 3185-3187.

4. Farooque Bashir Ansari, F. M. (2008). Potentiometric determination of stability constants of transition metal compolexes with p-aminobenzoic acid. *Int. J. Chem. Sci., 6* (2), 873-877.

5. Pulimadi R Reddy, P.R. (2007). Ternary complexes of cobalt cysteinylglycine with histidylserine and histidylphenylalnine-stabilities and DNA properties. *J. Chem. Sci., 119* (6), 603-612.

6. Paula Gamerio, C. R. (2007). Solution studies on binary and ternary complexes of copper with some fluoroquinolones and 1,10-phenanthroline: antimicrobial activity of ternary metalloantibioics. *International Journal of Pharmaceutics, 334*, 129-136.

7. Santosh Narayan Chadar, F. K. (2008). Electrochemical study and thermodynamic parameters of Cd(II) complexes with some antibiotics and vitaminB$_X$ system. *CHEMIJA , 19* (3-4), 1-6.