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STABILITY CONSTANTS OF BINARY AND TERNERY COMPLEXES OF IBUPROFEN AND PARACETAMOL

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ABSTRACT

The interaction of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) metal ions with ibuprofen (IBP) and paracetamol (PC) have been studied by pH-metric technique at 0.1 M (KNO_3) ionic strength at 302 ± 0.5 K in aqueous medium. The data obtained were used to evaluate the values of proton-ligand and metal-ligand stability constants using Irving-Rossotti titration technique. Mixed ligand complex studies of these metal ions using aspartic acid (ASP) and glutamic acid (GLU) as primary ligands and IBPand PC as secondary ligands also have been carried out pH-metrically at the same conditions.

Keywords: Ternary complexes, Transition metal ions, ibuprofen, paracetamol, aspartic acid and glutamic acid.

INTRODUCTION

Recently there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method[1-3]. The ligand ibuprofen (IBP) is well known for its analgesic actions and the ligand paracetamol (PC) has an analgesic and antipyretic actions[4-6].

Ternary complexes of Ni (II) and Cu (II) with nicotinic acid as primary ligand and imidazoles, benzimidazole, histamine and L-histidine as secondary ligands have been studied by Nair and Neekantan[7]. Patil and Mhaske[8] have studied the stability constants of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with nitrilotriacetic acid and Iminodiacetic acid as primary ligands and ibuprofen and paracetamol as secondary ligands potentiometrically. Nigam and coworkers[9] have studied the ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) using ASP as primary ligand and thymine as secondary ligand potentiometrically. Ternary complexes of Cu (II) using ASP and GLU as primary ligands have been reported potentiometrically by Pandeya and Patel[10]. Kalshetti and coworkers[11] have studies binary and ternary complexes of Co (II), Ni (II), Cu (II) and Zn (II). Mixed Ligand Complexes of Transition Metal (II) ions with N-(2-hydroxybenzylidene)-2, 3-dimethylaniline as Primary Ligand and N-(2-hydroxy-1-naphthylidene)-4-chloroaniline as secondary Ligand has been studied by Mapari and Mangaonkar[12]. Solution equilibrium of ternary systems involving transition metal ions, hydroxamic acids, and bioligands has been studied by Khalil and Mahmoud[13].

In this paper the stability constants of binary and ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) ions with ASP and GLU as primary ligands and IBP and PC as secondary ligand at 302 ±0.5 K and at fixed ionic strength, μ = 0.1M KNO_3 using modified form of Irving-Rossotti pH-metric technique[14] in aqueous medium have been studied. In case of ligand IBP the titration were carried out in40% (v/v) ethanol-water mixture.

EXPERIMENTAL

The ligand IBP was obtained from Genuine Chemicals Co. Mumbai and PC was of Zim laboratories, Kalmeshwar (Nagpur). The ligands were used as such. Ethanol was purified by standard method as described by Weissberer[15]. Carbonate free sodium hydroxide solution was prepared by standard method[16]. All other solutions were prepared in doubly distilled water.

The pH-metric measurements were carried out by using Elico digital pH-meter model L-120 with combined glass-calomel electrode with an accuracy of ± 0.01 of pH unit at

302 ± 0.5 K. the pH-meter was standardized against 0.05 M potassium hydrogen phthalate solution in acid medium and 0.01M borax solution in alkaline medium. The pH meter readings in 40% ethanol-water mixture were converted to (H+) values by applying correction proposed by Van Uitert and Haas[17].
For determination of proton-ligand stability constant of the secondary ligand and the metal-ligand stability constants of binary and ternary complexes, the following set of solutions were prepared and titrated against standard alkali solution.

Binary Systems
i. 9.6 X 10^{-3}M HNO_3
ii. 9.6 X 10^{-3}M HNO_3 + 4.0 X 10^{-3}M secondary ligand
iii. 9.6 X 10^{-3}M HNO_3 + 4.0 X 10^{-3}M secondary ligand +1.0 X 10^{-3}M metal ion.

Ternary Systems
i. 9.6 X 10^{-3}M HNO_3
ii. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M secondary ligand
iii. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M primary ligand +1.0 X 10^{-3}M metal ion
iv. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M primary ligand +1.0 X 10^{-3}M metal ion + 1.0 X 10^{-3}M secondary ligand

The ionic strength was maintained constant (0.1M) by adding required volume of 1M KNO_3. In case of IBP 40% ethanol-water mixture was maintain constant by adding required volume of ethanol. The ratio of metal (M): secondary ligand (L) was maintained at 1:5 in each of the binary systems and the ratio of metal (M): primary ligand (A): secondary ligand (L) was maintained at 1: 1: 1 in each of the ternary system.

RESULTS AND DISCUSSION

Proton-Ligand Stability Constants
The plots of volume of alkali (NaOH) against pH-meter readings were used to evaluate the proton-ligand stability constants of IBP. The deviation between free acid titration curve and secondary ligand titration curve was used to evaluate the formation functions, $\overline{n}_A$. The proton-ligand formation curves were then obtained by plotting the values of $\overline{n}_A$ versus pH-meter readings. From the graphs, the values of log K_1^H were evaluated by half integral method (method A) and point wise calculation method (method B) and presented in Table-1.
The pK value of IBP is due to dissociation of –COOH group and that of PC is due to dissociation of –OH group.

Table-: Proton-Ligand Stability Constants

Ligand	$\log K_1^H$	
	Method A	Method B
IBP*	5.34	5. 32
PC	9.67	9.65

*40%(v/v) ethanol-water

Metal-Ligand Stability Constants of Binary Complexes
The metal-ligand stability constants of binary complexes were evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes were absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds:
1. The metal titration curves showed displacement with respect to the ligand titration curves along the volume axis. This indicated the affinity of the ligand with metal ions which released protons and produced the volume difference ($V_3 – V_2$).

2. The color change of the ligand in presence of metal ions appeared showing the formation of new species.
3. The hydrolysis of the metal ions was suppressed due to complex formation and the precipitation did not appear during the titration.

From the ligand and metal titration curves the value of $\bar{n}$ and from that the values of pL were obtained. The formation curves obtained were used to evaluate the metal-ligand stability constants by method (A) and (B) and presented in Table 2. The green blue precipited was observed for [Cu (II)-IBP] system at pH$\cong$ 4.00.In case of Cu (II) and Zn (II), precipited was observed at the pH $\cong$ 8.00.
The variation of $\bar{n}$ was found to be 0 to 0.8 which indicated that the composition of complexes was 1:1 in solution. The Irving-Williams order[18, 19]of stability constants was followed.

Table-2: Metal – Ligand Stability Constants of Binary Complexes

Metal→ Ligand ↓	Log K									
	Mn(II)		Co(II)		Ni(II)		Cu(II)		Zn(II)	
	A	B	A	B	A	B	A	B	A	B
IBP*	2.58	2.57	2.59	2.61	2.71	2.73	-	-	2.63	2.64
PC	2.91	2.93	3.14	3.16	3.30	3.28	-	-	-	-

*40%(v/v) ethanol-water

Metal – Ligand Stability Constants of Ternary Complexes

The metal – ligand stability constants of the ternary complexes were evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes were absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds:

1. The ternary complex titration curves show the displacement with primary complex titration curves. The horizontal distance was measured between acid curve and the secondary ligand curve ($V_2 - V_1$) and subtracted through the horizontal distance between ternary complex curves and primary complex titration curves ($V_4 - V_3$) show the positive difference which proves the earlier released of protons in the formation of ternary complexes.
2. The hydrolysis of the metal ions was suppressed and precipitation did not result.The values of $\bar{n}$ vary from 0 to 0.8, thus confirming the formation of 1: 1: 1 mixed ligand complexes. The values of $\log K_{MAL}^{ASP}$ and $\log K_{MAL}^{GLU}$ have been evaluated from the formation curves ($\bar{n}$ vs. pL). At $\bar{n}$ = 0.5 in the formation curve, pL = log K. The metal- ligand stability constant of IBP as secondary ligand and ASP and GLU as primary ligand are presented in Table 3. The [Zn (II)-ASP/GLU-PC] complexes were not formed due to precipitation at pH $\cong$ 8.00.

Table-3: Metal – Ligand Stability Constants of Ternary Complexes

System	$\log K_{MAL}^{MA}$									
	Mn(II)		Co(II)		Ni(II)		Cu(II)		Zn(II)	
	A	B	A	B	A	B	A	B	A	B
[M (II)-ASP-IBP]*	3.15	3.16	3.42	3.41	3.52	3.50	3.79	3.79	3.33	3.32
[M (II)-GLU-IBP]*	3.29	3.28	3.34	3.35	3.51	3.50	3.75	3.76	3.43	3.42
[M (II)-ASP-PC]	3.78	3.79	3.88	3.89	3.83	3.84	4.33	4.34	-	-
[M (II)-GLU-PC]	3.86	3.85	4.08	4.09	4.20	4.22	4.38	4.39	-	-

*40%(v/v) ethanol-water

The Irving-Williams order[18, 19] of stability constants was observed in case of binary as well as ternary complexes which is-

Mn (II) < Co (II) <Ni (II) <Cu (II) > Zn (II)

This sequence of stability of complexes with respect to metal ion is due to deceasing atomic radius and increasing the second ionization potential.

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