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POTENTIOMETRIC STUDIES OF BINARY AND TERNARY COMPLEXES OF SOME TRANSITION METAL IONS WITH SOME MEDICINALLY IMPORTANT LIGANDS

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ABSTRACT

The interaction of Mn(II), Col(II), Ni(II), Cu(II) and Zn(II) metal ions with ampicillin (AMP) and cephalexin (CEP) have been studied by pH-metric technique at 0.1 M (KNO_3) ionic strength at 29± 0.5°C in aqueous medium. The data obtained were used to evaluate,pb values of proton-ligand and metal-ligand stability constants using Irving-Rossotti titration technique.

KEY WORDS: *pH-metric technique , aqueous medium.*

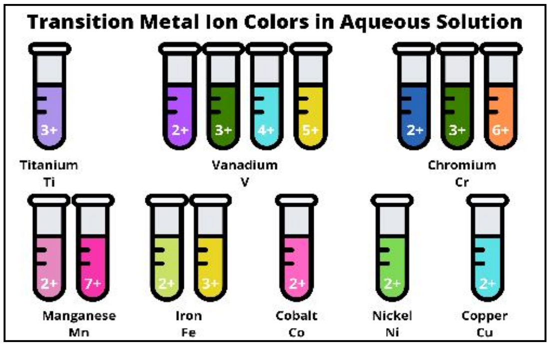
INTRODUCTION

Recently, there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method[1–5]. The ligands ampicillin (AMP) and cephalexin (CEP) are well known antibiotics. It was therefore interest to study the stability constants of binary and ternary complexes of these metal ions with these antibiotics at 29 ± 0.5°C and at μ=0.1 M KNO_3 employing modified form of Irving-Rosotti pH-metric technique'° in aqueous media.

MATERIAL AND METHODS :

All other solutions were prepared in doubly distilled water. pH measurements were carried out with Elico digital pH-meter model L-120 (accuracy ± 0.01) using glass-calomel electrode at 29 ± 0.5°C. The pH-meter was standardized against 0.05 M potassium hydrogen phthalate solution in acid medium and 0.01 M borax solution in alkaline medium.

For the determination of proton-ligand stability constant of the secondary ligands and metal-ligand stability constants of the binary and ternary complexes, the following sets of solutions were prepared and titrated against standard alkali solution.



Binary Systems

i. 9.4×10^{-3}M HNO_3
ii. 9.4×10^{-3}M HNO_3 + 4.0×10^{-3}M secondary ligand
iii. 9.4×10^{-3} M HNO_3 + 4.0×10^{-3}M secondary ligand + 1.0×10^{-3} M metal ion.

Ternary Systems

i. 9.4×10^{-3}M HNO_3
ii. 9.4×10^{-3}M HNO_3 + 1.0×10^{-3} M secondary ligand

iii. 9.4 × 10^{-3}M HNO_3 + 1.0 × 1.0 × 10^{-3} M primary ligand + 1.0×10^{-3} M metal ion.
iv. 9.4 × 10^{-3}M HNO_3 + 1.0 × 1.0 × 10^{-3} M Metal ion + ligand+1.0×10^{-3} M metal ion. + 1.0 × 10^{3} M secondary ligand.

The ionic strength was maintained constant (0.1 M) by adding required volume of 1M KNO_3. The ratio of metal (M) : secondary ligand (L) was maintained at 1:4 in each of the binary system and the ratio of metal (M) : primay ligand (A) : secondary ligand (L) was maintained at 1:1:1 in each of the ternary system.

RESULTS AND DISCUSSION

The plots of volume of alkali (NaOH) against pH-meter readings were used to evaluate the proton-ligand stability constants of AMP and CEP. The deviation between free acid titration curve and secondary ligand titration curve was used to calculate the formation functions η_A using Irving. Rossotti exprressionw. The proton-ligand formation curves were then obtained by plotting the values of η_A vs pH. From the graphs, the values of log K^H (pK) for AMP and CEP were determined by half integral (method A) and point wise calculation method (method B) and presented in Table 1.

Table-1: Determination of proton-ligand stability constants

Ligands	Constants (pK)	
	Method (A)	Method (B)
AMP	7.34	7.35
CEP	7.40	7.40

Metal-ligand stability constants

The metal-ligand stability constants were caluculated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydroxyl bearing complexes were absent. An examination of titration curves indicate that complexes formation have taken place in solution, on the following grounds.

1. The metal titration curves show displacement with respect to the ligand titration cuves along the volume axis. This indicate that the affinity of ligand with metal ions which release the protons and produce the volume difference (V_3-V_2).
2. The hydrolysis of metal ion was suppressed due to complex formation and the precipitation did not appeared during titration.

Table-3: Determination of metal-ligand stability constants of ternary complexes

Systems	**Constants (log K)**									
	Mn(II)		**Co(II)**		**Ni(II)**		**Cu(II)**		**Zn(II)**	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
[Mn(II)-NTA-AMP]	3.32	3.32	3.32	3.35	3.75	3.74	3.96	3.95	3.45	3.43
[M(II)-IMDA-AMP]	3.61	3.61	3.92	3.91	3.96	3.95	4.10	4.10	3.96	3.95
[M(II)-NTA-CEP]	3.81	3.80	3.85	3.85	4.06	4.10	4.15	4.18	3.65	3.84
[M(II)-IMDA-CEP]	3.85	3.84	4.03	4.06	3.90	3.91	4.30	4.28	3.94	4.00

C.The colour change of the ligand in presence of metal ions appeared during titration showing the formation of new species. From the ligand and the metal titration curves the values of ri and from that the values of pL (log K) were calculated. The formation curves obtained were used to calculate the metal-ligand stability constants by methods (A) and (B) presented in Table 2.

The variation of η was found to be 0 to 2 except for [Zn(II)-AMP], [Mn(II)-CEP] and [Zn(II)-CEP] systems where it was 0 to 1. This indicates the formation of 1:2 complexes for all system except [Zn(II)-AMP], [Mn(II)-CEP] and [Zn(II)-CEP] where the composition of complexes was 1:1 in solution. From table 2, it was observed that the metal-ligand stability constants of CEP were greater with respect to AMP. The Irving-Williams order of stability constants was followed by both ligands with metal ions.

Metal-ligand stability constant of ternary complexes

The metal-ligand stability constants of the ternary complexes were calculated assuming that the formation of the hydroxy products, polynuclear complexes, hydrogen and hydroxyl bearing complexes were absent. An examination of the titration curve indicated that ternary complexes formation have taken place in solution on the following grounds.

1.The mixed ligand titration curves show displacement with primary complex titration curves. The horizontal distance measured between free acid curves and secondary ligand curves (V_2-V_1) and subtracted through the horizontal distance between mixed ligand titration curves and primary complex titratin curves (V_4-V_3) show positive difference which proves the liberation of additional protons, which was a measure of mixed ligand formation.

2.The hydrolysis of metal ions was suppressed and precipitation did not results.

The values of n do not exceed 0.9. Thus confirming the formation of 1:1:1 mixed ligand complexes. The values of $\log_{MAL}^{NTA}$, and $\log_{MAL}^{IMDA}$ have been evaluated from the formation curves (η vs pL). At η = 0.5 in the formation curves pL = log K. The metal-ligand stability constants of transition metal ions with AMP and CEP as secondary ligands and NTA and IMDA as primary ligands are presentd in table 3.

Table-2: Determination of metal-ligand stability constants of binary complexes

Systems	Log K_1		Log K_2		Log K_3	
[Mn(II) - AMP]	3.04	3.08	2.85	2.82	5.94	5.95
[Co(II) - AMP]	3.20	3.21	2.86	2.86	6.06	6.05
[Ni(II) - AMP]	3.44	3.49	3.05	3.05	6.51	6.54
[Cu(II) - AMP]	3.86	3.90	3.25	3.26	7.12	7.14
[Zn(II)- AMP]	2.64	2.66	–	–	–	–
[Mn(II)- CEP]	2.73	2.76	–	–	–	–
[Co(II) - CEP]	3.36	3.40	3.04	3.05	6.42	6.45
[Ni(II) - CEP]	3.44	3.45	3.17	3.16	6.61	6.61
[Cu(II) - CEP]	4.64	4.64	4.26	4.24	8.92	8.90
[Zn(II) - CEP]	2.74	2.75	–	–	–	–

In general, the metal-ligand stability constant values were in accordance with Irving-Williams order. Higher stability of [Co(II)=IMDA-CEP] complex was observed as compared to that of [Ni(II)-IMDA-CEP] complex.

CONCLUSION :

The aim of the study was to know the effect of binary and ternary complex as compared to plain drug is different or the same. This part of application is in progress as it is time consuming.

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