



THE EFFECT OF SOLVENT ON STABILITY CONSTANT OF MIXED LIGAND COMPLEXES

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ABSTRACT

p^H – metry have been used most widely for the simultaneous equilibrium of transition metals with different amino acids like Histidine, Glutamic acid, Proline and L-aspartic acid using aqua-organic solvents. The ionic strength was maintained and complex formation was observed.

Key Words: p^H – metry, transition metals, amino acids.

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INTRODUCTION

The determination of the stability constant is of paramount importance in the knowledge of Chelates. The mixed ligand complexes plays an important role in numerous chemical and biological systems. Potentiometric study of mixed ligand system was made by Irving-Rossotti titration technique in NaClO₄ ionic strength and the values obtained were found to be in good agreement with literature values reported¹⁻².

J. Bjerrum and Ido Leden's work enlightened the interest in the investigation of equilibrium between metal- ligand. Schwarzenback and Ackermann³ found that stability of Chelates decreases as the size of ring increases.

The stability constant gives the formation of metal-ligand. Metal ions plays vital role in the formation of stable complexes is of interest to the analytical chemists and bio-inorganic researchers.

The present communications we selected the metal ions Mn, Fe and Ni with amino acids Histidine, Glutamic acid, Proline and L-aspartic acid.

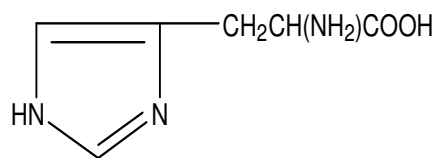
EXPERIMENTAL

All the chemicals selected for present communications are obtained from SD – fine chemicals. The chemicals NaOH, perchloric acid, sodium perchlorate metal ions and ligands were prepared in glass distilled water and alcohol used also distilled. The titrations were carried out at 25 ± 0.5 and inert atmosphere were maintained by bubbling oxygen free nitrogen gas throughout the course of technique. Stability constant of these ligands were determined by Irving Rossotti techniques⁴. For p^H-titrations, the following sets of solutions were prepared and titrated with 0.2M NaOH solution.

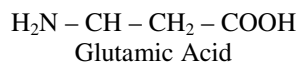
RESULT AND DISCUSSION

The present study has great importance as formation constant of amino acid complexes in many biological processes. The potentiometry may be considered as the most accurate method for evaluation of complex equilibrium constant. Literature survey reveals that many workers studied the complexation. The ionic strength was maintained to 1.0M with NaClO₄. The metal-ligand ration was 1:5. The metal-ligand stability constant indicates that in 50% ethanol-water solution showing higher values. The binary titrations keeping 1:5 metal to ligand ratio and for ternary systems keeping 1:5:5 metal to ligand ratios were observed. There are various interacting forces presents when we use solvent mixtures. The statistical data of Δ log K for ligands were observed.

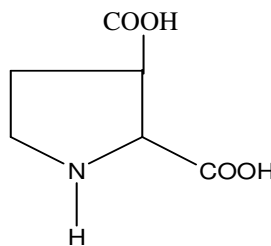
Structure of amino acids are given as:



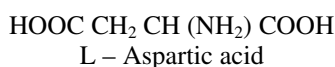
Histidine



Glutamic Acid



Proline



L - Aspartic acid

Table-1: Protonation constant of ligands

Ligands	Aqueous Solution		50% ethanol – water		100% ethanol solutions	
	Log K_1^{H}	Log K_2^{H}	Log K_1^{H}	Log K_2^{H}	Log K_1^{H}	Log K_2^{H}
Histidine	3.81	7.21	5.89	8.60	2.3	7.2
Glutamic acid	3.12	6.01	6.32	10.14	3.61	6.1
Proline	3.23	4.19	4.0	9.09	3.08	4.9
L – aspartic acid	4.01	7.90	3.60	8.29	3.90	2.69

Table-2: Metal Ligand Stability Constant

Metal ions	Aqueous				50% ethanol – water				100% ethanol solution			
	Histidine	G.A.	Proline	A.A.	Histidine	G.A.	Proline	A.A.	Histidine	G.A.	Proline	A.A.
Mn	4.92	4.09	3.81	3.03	7.12	5.12	5.05	11.02	2.16	3.66	3.10	4.92
Fe	5.16	5.9	4.92	6.12	4.69	7.21	8.61	7.69	3.90	5.02	2.98	3.16
Ni	3.10	6.1	3.66	5.10	6.10	6.73	7.22	6.27	2.69	4.18	3.08	4.01

Stability constant of Mixed-Ligand complexes of Mn, Fe & Ni with amino acid such as Histidine, Glutamic acid, Proline and L-aspartic acid studied in the ratio of 1:5:5. The stability constant lies in the range of 4:0 – to 11:00.

The mixed ligand complexation of Mn, Fe & Ni with Histidine as a primary ligand and Glutamic acid, Proline and L-aspartic acid as secondary ligands are selected.

Ternary complexes of Co(II) with amino acids show positive log K values which gives them extra stability⁵.

The metal-ligand stability constant indicates that in ethanolic solution at 50% ethanol + water shows higher values. It is reported that P^{K_1} of amino acid increased as the concentration of ethanol increases⁶.

The study of transition metals with pyrazoline by p^{H} - metric methods, the complexes are between Co(II), Ni(II) and Cu(II) with pyrazoline occurred simultaneously due to the presence of $-\text{OCH}_3$ group⁷.

The present work shows the stability constants for mixed-ligand complexes are in the range of 4:00 to 11:00 and confirmed the complexation between metal and amino acids⁸.

The $\Delta \log K$ values are positive. It shows that primary and secondary ligands forms the ternary complexes.

Table-3: Stability Constant of Mixed Ligand Complexes

Metal ions	Aqueous		
	Mixed ligand system	Log K _{MXY}	$\Delta \log K$
Mn (aq.)	Histidine + Glutamic acid	10.70	2.30
	Histidine + Proline	8.76	0.99
	Histidine + Aspartic acid	6.016	1.23
Fe (aq.)	Histidine + Glutamic acid	5.63	1.0
	Histidine + Proline	5.25	2.51
	Histidine + Aspartic acid	7.19	0.82
Ni	Histidine + Glutamic acid	10.02	2.01
	Histidine + Proline	7.92	1.91
	Histidine + Aspartic acid	6.30	0.79

Metal ions	50% ethanol – water		
	Mixed ligand system	Log K _{MXY}	$\Delta \log K$
Mn (aq.)	Histidine + Glutamic acid	10.61	3.16
	Histidine + Proline	9.23	2.30
	Histidine + Aspartic acid	10.0	2.82
Fe (aq.)	Histidine + Glutamic acid	8.76	0.98
	Histidine + Proline	7.10	3.90
	Histidine + Aspartic acid	7.89	2.60
Ni	Histidine + Glutamic acid	7.70	2.13
	Histidine + Proline	6.9	3.03
	Histidine + Aspartic acid	9.09	2.51

Metal ions	100% ethanol system		
	Mixed ligand system	Log K _{MXY}	$\Delta \log K$
Mn (aq.)	Histidine + Glutamic acid	6.16	1.96
	Histidine + Proline	5.02	1.00
	Histidine + Aspartic acid	5.21	2.10
Fe (aq.)	Histidine + Glutamic acid	4.79	0.97
	Histidine + Proline	6.03	2.0
	Histidine + Aspartic acid	5.72	1.00
Ni	Histidine + Glutamic acid	5.18	0.96
	Histidine + Proline	4.91	2.01
	Histidine + Aspartic acid	4.71	2.25

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