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Mixed Ligand Complexes of Amino Acids

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Introduction:

Mixed ligand formation equilibria of metal ion such as Fe (III) with amino acids is of great importance. Fe (III) is the transition metal ion having vacant d-orbitals. Amino acids act as a ligand which forms binary and ternary complexes which play a vital role in detoxification and drug desigining [(1)]. Mixed-ligand complexes are formed in solutions containing metal ion with two or more same or different ligands. Many researchers worked on the stability of mixed-ligand complexes [(2)].

During the past decades, di-amines and their derivative have been studied and have many applications in the field of biochemistry, biotechnology and environmental science [(3)]. The functional group of amino acids are similar to those of enzyme are – COOH, – NH_2 etc. are very important for many type of biological and analytical reactions [(4)]. The present study deals with an equilibrium study on the mixed ligand complex formation of Fe (III) in aqueous medium at a constant ionic strength 0.1M $NaNO_3$ at room temperature.

Stability of mixed-ligand complexes of Fe (III) with some amino acids may be influenced by various factors such as size of ligand, size of chelate ring, basicity etc. For present study we have selected amino acids and Fe (III).

Experimental:

All the chemicals used for titration were of Sd-fine chemical ltd. All the chemicals used for pH-metric measured are prepared in glass distilled water such as amino acids, metal ion solution, sodium hydroxide etc.

The following solutions are prepared (total volume 50ml) and titrated potentiometrically against standard NaOH (0.2N) solution.

a) HNO_3 (2ml) + $NaNO_3$ (2ml)
b) HNO_3 (2ml) + Ligand (2ml) + $NaNO_3$ (2ml)
c) HNO_3 (2ml) + Ligand (2ml) + Metal solution (2ml) + $NaNO_3$ (2ml)

pH-metric titrations were carried out by using ELICO digital pH-meter with combined electrode. The relative stabilities of the mixed ligand complexes formed are measured by adopting Irving-Rossotti technique [(5)].

Result & Discussion:

The present study has great importance in co-ordination chemistry dealing with ligand and metal ions. The complex of Fe (III) formed are in the 1:1 and 1:1:1 in the binary and ternary system. Several workers [(6-7)] studied in the field of complex formation involving transition metal, inner transition metals with different types of ligand. The method adopted for calculation cannot give direct calculation of equilibrium concentration.

For the present study we have selected few amino acids, the pH-metric titrations were carried out keeping 1:1 metal-ligand ratio.

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Table No. 1: Proton-ligand stability

Vaniline			Phenylalanine			Histidine			Phenylalanine			Histidine		
pH	$\bar{\eta}_A$	P^{K_1}	pH	$\bar{\eta}_A$	P^{K_1}	pH	$\bar{\eta}_A$	P^{K}	pH	$\bar{\eta}_A$	P^{K_2}	pH	$\bar{\eta}_A$	P^{K_2}
4.72	0.62	4.83	10.72	0.63	11.28	10.70	0.60	10.89	8.63	1.61	8.84	8.10	1.62	8.28
4.74	0.59	4.86	10.74	0.58	11.19	10.72	0.56	10.88	8.64	1.58	8.83	8.11	1.62	8.29
4.76	0.55	4.96	10.76	0.53	11.12	10.74	0.54	10.86	8.65	1.56	8.82	8.12	1.59	8.30
4.78	0.52	5.02	10.78	0.50	11.02	10.76	0.53	10.85	8.66	1.55	8.84	8.13	1.56	8.32
5.0	0.50	5.04	11.0	0.49	10.96	10.78	0.50	10.88	8.67	1.52	8.86	8.14	1.55	8.33
5.02	0.48	5.04	11.02	0.48	10.80	11.00	0.49	10.90	8.68	1.51	8.87	8.15	1.54	8.35
5.04	0.46	5.06	11.04	0.47	10.79	11.02	0.47	10.92	8.69	1.50	8.89	8.16	1.52	8.37
5.06	0.42	5.07							8.70	1.49	8.90	8.17	1.50	8.39

Table No. 2: Pointwise Calculation of Prolonation Constant

Ligand	Half-Integral Method		Point-wise Method	
	P^{K_1}	P^{K_2}	P^{K_1}	P^{K_2}
Vaniline	5.03	-	5.01	-
Phenylalanine	10.95	8.84	10.86	8.51
Histidine	10.80	8.76	10.78	8.23

The proton-ligand stability constant of Ascorbic acid with transition metals V^{+2}, Cr^{+2}, Fe^{+3} at ionic strength 0.1M, 0.3M, 0.6M $NaClO_4$ in aqueous medium shows the dissociation of two enolic – OH group. The first P^K values is 4.16 which is due to dissociation of – OH and second at P^K value is 11.54 which is higher than first P^K value. In these cases the effect of increase of ionic strength from 0.1M, 0.3M to 0.6M decreases the P^K value [6].

The mixed-ligand complexation of Fe (III) with Vaniline, Phenylalanine and Histidine, the ratio is of 1:1:1. The results of stability constant are in the range of 4.30 to 6.00.

Table No. 3: Stability constant of Mixed-ligand complexes

Metal ion	Mixed-Ligand system	log Kmxy	Δ log k
Fe (III)	Vaniline + Phenylalanine	4.39	1.09
	Vaniline + Histidine	5.89	2.60

The structure flexibility of Cu (II) binary complexes is expected to favour mixed ligand co-ordination with nucleic acids [7]. All the chelates formed in simultaneous equilibria by taking M:X:Y in the ration of 1:1:1.

In the present study we observed a increasing trend in the log KMXY value of the metal-ligand chelates as reported early also [8]. For the ternary complexes Δ log k values observed are positive indicating the formation of the complexes.

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