Formation Constants of Ternary Complexes of Cu(II) with N-Substituted Anthranilic Acids & Some Amino Acids†

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Formation of constants of binary and ternary complexes of the systems of the type ML and MAL, where M = Cu^{2+}; A = glycine, α-alanine, phenylalanine, proline, hydroxyproline; and L = N-methylanthranilic acid, N-phenylanthranilic acid have been determined potentiometrically at 30°, 40°, 50°C and ionic strength = 0.1 M(KNO$_3$) in 50% (v/v) aqueous ethanol medium. The order of stabilities of ternary complexes have been compared with those of corresponding binary complexes and results are discussed on the basis of Δlog K, the difference between the stabilities of ternary and binary complexes. The entropy values have been found to be favourable for ternary complex formation.

It is generally observed from a literature search that the stability constants of complexes of N-methylanthranilic acid with bivalent metal ions are higher than those of N-arylanthranilic acids. Presently we have determined the formation constants of the ternary complexes of Cu(II) with N-methyl- and N-phenylanthranilic acids and various amino acids such as glycine, α-alanine, phenylalanine, proline and hydroxyproline at different temperatures and ionic strength = 0.1 M, potentiometrically in 1:1(v/v) ethanol-water medium using well known equations[1-3]. The enthalpy and entropy (ΔH and ΔS) values associated with the complex forming reactions have also been calculated.

All the chemicals used were of AR grade. N-Methyl- and N-phenyl-anthranilic acids were prepared in laboratory. The solutions were prepared in doubly distilled water. The ligand solutions were prepared in purified ethyl alcohol. Following sets of solutions were prepared and titrated pH-metrically against standard potassium hydroxide (0.1 M) under N$_2$ atmosphere: (A) Acid (4×10^{-3} M); (B) Acid + N-Sub.An.A. (2×10^{-3} M); (C) Acid + amino acid (2×10^{-3} M); (D) Acid + N-Sub.An.A + Cu(II) ($2 \times 10^{-3} M$); (E) Acid + amino acid + Cu(II); and (F) Acid + N-Sub.An.A. + amino acid + Cu(II). (In sets

B, D and F N-Sub.An.A. refers to N-methyl- or N-phenyl-anthranilic acid).

The total volume of each system in 1:1 (v/v) aqueous ethanol was kept at 50 ml. The pH correction factor was obtained for 1:1 (v/v) ethanol-water composition following the procedure of Gentile and Dadgar[4,5]. The titrations of the ternary systems were carried out at 30°, 40° and 50°C and at constant ionic strength (0.1 M).

Formation of ternary complexes has been inferred from a shift in pH of precipitation and with a colour change or intensification of colour of solution[6]. The 1:1:1 curve did not coincide with either of the two binary curves (ML or MA). It appeared below the 1:1 metal-ligand curves of both the ligands, indicating the simultaneous formation of mixed complex. This was further confirmed by almost identified pH ranges of complexation of Cu(II) with N-Sub.An.A and of Cu(II) with amino acids.

The dissociation constants of the N-substituted anthranilic acids and the formation constants of binary complexes were redetermined under present experimental conditions using the method of Irving and Rossotti. The values thus obtained (Table 1) were found to be in good agreement with literature values. The order of formation constants of the ternary complexes is the same as that of the binary complexes of the ligands (N-Me-An.A. and N-Ph.An.A) (Table 2). However, the values K^M_{MAL} are significantly lower than the values of the first formation constants K^M_{MA} and K^M_{ML} of the binary complexes. The Δlog K values were calculated and are negative for all systems (Table 2).

In Cu(II)-N-Me-An.A- amino acid systems, the Δlog K values are higher than those of the Cu(II)-N-Ph.An.A- amino acid systems. This may be due to steric hindrance of the bulkier phenyl group. With respect to amino acids the high Δlog K for phenylala-

Table 1—Stability Constants* of Binary Complexes

[Ionic Strength = 0.1 M; temp = 30°C]

Ligand	pK_a	Cu(II) log K
N-Me.An.A	5.62	3.94
N-Ph.An.A	5.10	3.03
Glycine	9.29	8.82
Alanine	9.44	8.86
Phenylalanine	8.72	8.56
Proline	10.11	9.41
Hydroxyproline	9.33	9.11

* Constants are accurate within ± 0.04

Table 2—Stability Constants* of
Ternary Complexes of Cu(II)

Ligand	Log K (N-Me.An.A)	$\Delta \log K$	log K (N-Ph.An.A)	$\Delta \log K$
Glycine	9.35	−3.41	8.23	−3.62
α-Alanine	9.21	−3.59	8.04	−3.85
Phenylalanine	9.74	−2.76	8.50	−3.09
Proline	9.25	−4.10	8.08	−4.36
Hydroxyproline	9.89	−3.16	8.62	−3.52

* Constants are accurate within ±0.07

Table 3—Thermodynamic Parameters of
Ternary Complex Formation of Cu(II)

[Ionic strength = 0.1 M; temp = 30°C]

Ligands	$+\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1}deg^{-1})
N-Me.An.A.-Gly	40.38±0.31	53.99±0.17	311.45±0.46
N-Me.An.A.-Ala	36.15±0.43	53.17±0.12	294.78±1.02
N-Me.An.A.-Ph.Ala	43.07±0.36	56.25±0.17	327.78±0.63
N-Me.An.A.-Pro	39.51±0.50	53.45±0.15	306.79±1.15
N-Me.An.A.-OH.Pro	38.33±0.20	57.12±0.10	315.01±0.33
N-Ph.An.A.-Gly	42.13±0.29	47.56±0.17	296.00±0.39
N-Ph.An.A.-Ala	36.78±0.35	46.45±0.15	274.68±0.66
N-Ph.An.A.-Ph.Ala	56.67±0.27	49.12±0.15	349.14±0.39
N-Ph.An.A.-Pro	49.84±0.45	46.70±0.15	318.61±0.98
N-Ph.An.A.-OH.Pro	64.91±0.24	49.80±0.12	378.58±0.39

nine is due to the presence of phenyl group which increases the π-acceptor capacity of phenylalanine favouring the formation of ternary system. The higher $\Delta \log K$ value for hydroxyproline system as compared to that of proline system is due to more basic character of proline which decreases the magnitude of positive charge on metal ion. Hence ternary complex formation is more favourable in hydroxyproline. The lower stability of proline system, in comparison to those of glycine and alanine systems can be explained on the basis of cyclic structure of proline.

The positive values of ΔH and negative values of ΔG (Table 3) indicate that the reactions are endothermic and spontaneous in nature. Though positive enthalpy changes in all the systems point to weak metal-ligand bonds and indicate that the enthalpy change does not favour the complexation, the corresponding higher ΔS values are responsible for the formation of complexes.

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