Equilibrium Studies on Mixed Ligand Complexes of Kojic acid, Maltol or Acetyl acetone in presence of N-N donors - pH metry

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Kojic acid, maltol and acetyl acetone coordinate as secondary ligands with Co(II), Ni(II), Cu(II) Zn(II) and Cd(II) ions in presence of bipyridyl or 1,10-phenanthroline.

The metal complexes of substituted 3-hydroxy-4-pyrone are receiving more and more attention because of the industrial and biological importance [1-9]. The effectiveness of hydroxy pyrone to act as metal binding species is attributed to its (a) capability to form both σ and π bonds with metal ions and (b) availability of donor groups at physiological pH. As a part of the programme [10,11] of investigating the coordinating tendencies of 3-hydroxy-2-methyl-pyran-4-one (maltol), 3-hydroxy-6-(hydroxymethyl)-pyran-4-one (kojic acid) and acetyl acetone, formation constants of ternary complexes of type MLA are determined in aqueous medium using potentiometry (where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), L = kojic acid or maltol or acetyl acetone, A = bipyridyl or 1,10-phenanthroline).

EXPERIMENTAL

The ligands - kojic acid (KA), maltol (MA) and acetyl acetone (AA) - are obtained from Fluka (Switzerland). The other ligands - bipyridyl and 1,10-phenanthroline - are obtained from Aldrich Chemical Company Ltd., (U.S.A.). The metal salts of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are of AnalaR grade and their solutions are standardized volumetrically by titration with the sodium salt of EDTA [12]. Potentiometric measurements are carried out at 30°C in aqueous medium (with 0.1 M KNO_3 as background electrolyte) using control dynamics pH meter. The pH meter readings are plotted against **a** (moles of base added per mole of ligand) or **m** (moles of base added per mole of metal ion). Calculations are carried out with the help of computer program - BEST [13].

RESULTS AND DISCUSSION

The potentiometric titration curves (Fig.1) of 1:1:1 [Ni(II)-bipy-maltol] show a steep inflection at m = 1 followed by another inflection at m = 2. The ternary curve coincides with binary curve upto m = 1 where 1:1 [Ni(II)-bipy] complexes are formed. This indicates that only 1:1 [Ni(II)-bipy] complex is formed in the region m = 0 to m = 1 and maltol does not coordinate with Ni(II) ion in this region. The divergence of mixed ligand curve from the binary [Ni(II)-bipy] curve beyond m = 1 suggests the coordination of maltol as a secondary ligand. Hence the formation of ternary complexes can be considered to occur in stepwise equilibria.

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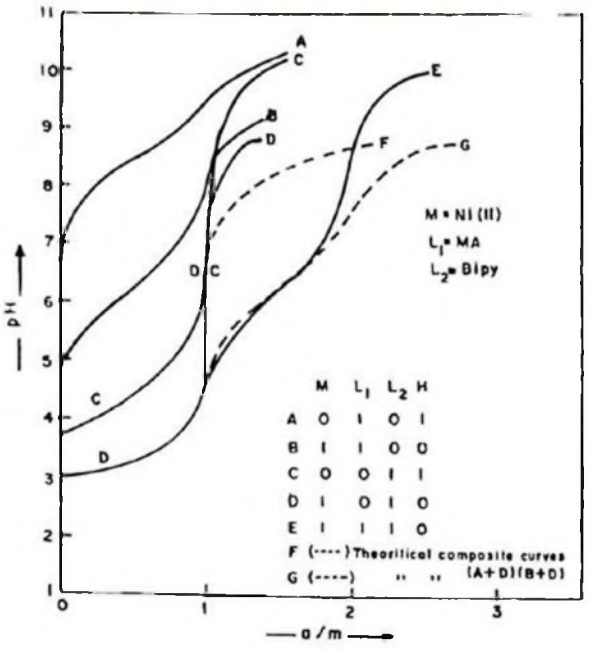


Fig 1 Potentiometric Titration Curves of Ni(II) Ternary Complex involving Maltol & Bipyridyl

$$Ni(II) + bipyH^{+} \rightleftharpoons [Ni(II)\text{-}bipy] + H^{+} \quad \ldots (1)$$

$$[Ni(II)\text{-}bipy] + MAH \rightleftharpoons [Ni(II)\text{-}bipy\text{-}MA] + H^{+} \quad \ldots (2)$$

where MAH = maltol / kojic acid / acetyl acetone.

The formation of ternary complexes is supported by non-superimposable nature of the theoretical composite curve over the experimental mixed ligand curve. Similar types of graphs are obtained in the case of other systems under study.

The potentiometric titration curves for Cu(II) :ligand1 :ligand2 in the ratio 1:1:1 show a single inflection at m = 2 suggesting the

Table 1

Formation Constants of Complexes with Some Bivalent Metal Ions

[for addition a = bipy or phen; L = kojic acid/ maltol / acetyl acetone in Binary and Ternary Complexes]

T = 30°C; I = 0.1 M KNO_3; Medium - Aqueous

Ligands	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
Formation constant (log K_{ML}^{M}) of Binary Complexes					
KA(pK_a=7.62±0.06)	4.75 ± 0.05	4.93 ± 0.03	6.57 ± 0.05	5.14 ± 0.04	4.48 ± 0.06
MA(pK_a=8.55±0.01)	5.35 ± 0.08	5.57 ± 0.05	7.61 ± 0.03	5.77 ± 0.03	5.15 ± 0.05
AA(pK_a=8.87±0.05)	5.02 ± 0.01	5.60 ± 0.06	7.87 ± 0.01	4.76 ± 0.07	3.59 ± 0.08
Step Constant (log K_{MAL}^{MA}) of Ternary Complexes					
Bipy + KojicA	4.68±0.06	5.04±0.03	6.73±0.02	5.04±0.06	4.33±0.02
Phen + KojicA	4.69±0.03	4.98±0.03	6.48±0.02	5.01±0.05	4.30±0.06
Bipy + Maltol	5.43±0.02	5.72±0.01	7.80±0.06	5.71±0.03	5.03±0.04
Phen + Maltol	5.31±0.01	5.59±0.07	7.70±0.03	5.64±0.05	4.99±0.05
Bipy + Acetyl	4.90±0.03	5.36±0.01	7.78±0.08	4.56±0.05	3.28±0.02
Phen + Acetyl	4.87±0.05	5.26±0.04	7.75±0.06	4.50±0.05	3.08±0.02

In the case of Ternary complexes of Cu(II), the log K_{MAL}^{M} values obtained are converted into log K_{MAL}^{MA} for better comparison.

Table 2

Comparison of Δlog K (& %R.S. Values in Parenthesis) for Ternary Complexes with Some Bivalent Metal Ions

T = 30°C; I = 0.1 M KNO_3; Medium - Aqueous

Ligand	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
Bipy+KA	-0.07(-1.47)	+0.11(+2.23)	+0.16(+2.43)	-0.10(-1.94)	-0.15(-3.35)
Phen+KA	-0.06(-1.26)	+0.05(+1.01)	-0.09(-1.37)	-0.13(-2.53)	-0.18(-4.02)
Bipy+MA	+0.08(+1.49)	+0.15(+2.69)	+0.19(+2.49)	-0.06(-1.04)	-0.12(-2.33)
Phen+MA	-0.04(-0.75)	+0.02(+0.36)	+0.09(+1.18)	-0.13(-2.25)	-0.16(-3.10)
Bipy+AA	-0.12(-2.39)	-0.24(-4.28)	-0.09(-1.14)	-0.20(-4.20)	-0.31(-8.63)
Phen+AA	-0.15(-2.98)	-0.34(-6.07)	-0.12(-1.52)	-0.26(-5.46)	-0.51(-14.2)

release of two protons simultaneously (from both ligands). Such equilibria are represented by equation 3.

$$Cu(II) + bipyH^{+} + MAH \rightleftharpoons [M\text{-}bipy\text{-}MA] + 2\,H^{+} \quad \ldots\ldots (3)$$

The data in Table 1 & 2 show that the stability with respect to the primary ligands in ternary complexes is in the order: bipyridyl > 1,10-phenanthroline. Similarly, the stability order with respect to the secondary ligands in these systems is: maltol > kojic acid > acetyl acetone. The ternary formation constants of bivalent metal ions is in the order Cu(II) > Ni(II) > Co(II) < Zn(II) < Cd(II).

Perusal of ΔlogK values and % R.S. values in Table 2 indicates positive values for most of the systems studied; when there are negative values, they are less than -0.4, the value obtained on statistical grounds alone. In other words, some positive effect is operating in these sysems which is responsible for getting positive or less negative ΔlogK values.

Sigel [14] considered that coordination of the strong field ligand like bipy or phen makes the metal ion in 1:1 complex [like Cu(Bipy) (H_2O)] somewhat more distorted to square planar geometry, thus creating the right geometry for the coordination of the secondary ligand. He has proposed that the positive effect is especially favoured when secondary ligand is oxygen O^{-}-O^{-} donor. In such cases, the K_{MAL}^{MA} values are more than K_{ML}^{M} values resulting in positive ΔlogK values. He explained this effect in terms of metal - ligand π interactions.

Though the basicity of phen is higher than that of bipy, the formation constants $\log K_{MAL}^{MA}$ of [M(II)-bipy-KA/MA/AA] are higher than those of [M(II)-phen-KA/MA/AA]. This is because of stereochemical factors. The rigidity of pyridyl rings of phen

may not permit to have maximum interaction through the overlap of the orbitals between the ligand and metal ion. However, bipy being a flexible molecule (with two pyridyl rings connected by a single bond), such interaction may be facilitated by moving the two donor atoms apart maintaining the planarity of molecule.

The sequence of stability of ternary complexes with respect to secondary ligands decrease in the order maltol > kojic acid > acetyl acetone. In view of greater basicity of enol group of acetyl acetonate ligand and its resonance stabilization of the heterocyclic chelate ring of a acetyle acetonate complexes, one expects acetyl acetone to form relatively more stable complexes. But the experimental value is in the reverse. The probable reason could be lack of formation of metal to ligand π bond in ternary complexes involving acetyl acetone.

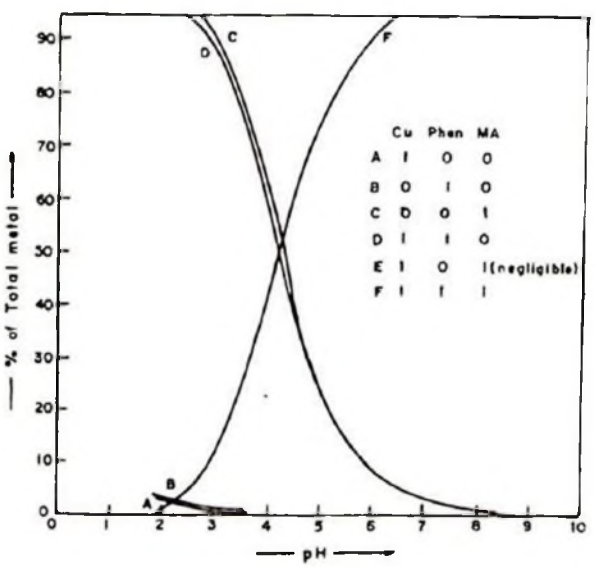
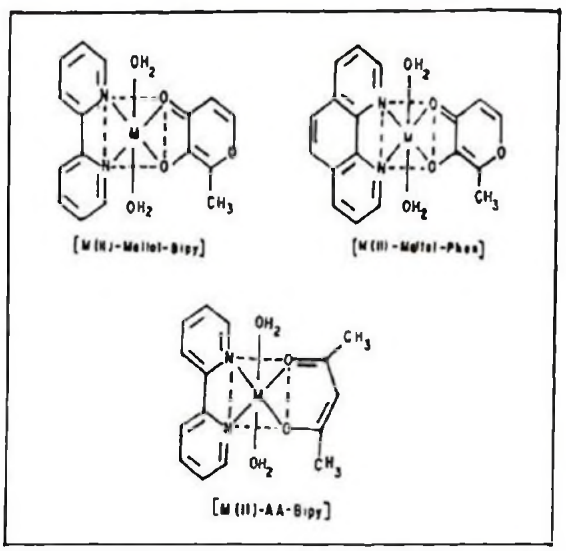


Fig 2 - BEST (SPE) Computed Distribution of Complex Species with pH
Cu(II) - Maltol-Phen Ternary System

The stability constants of ternary complexes of bivalent metal ions is in the order: Cu(II) > Ni(II) > Co(II) < Zn(II) < Cd(II). This order is in conformity with Irving - William's natural order of stabilities [15].

The probable structures of the Ternary complexes containing bipy or phen with maltol or AA is shown schemetically as below.



BEST (SPE) computed distribution diagram (of total metal among the various metal-ligand species and pH) for Cu(II) ternary systems involving maltol and phen is shown in Fig.2. At pH 2, the predominant species is Cu(II)-phen. The free ligand (maltol) is present to the extent of 100% at pH 2. From pH 3 onwards, ternary complexation starts while % of Cu(II)-phen complex reaches its minimum at pH 6. In higher pH region, only ternary species are present. From this distribution diagram, it is concluded that ternary complexation takes place in stepwise fashion in which phenanthroline acts as primary ligand and maltol acts as secondary ligand as is shown through equations 1 and 2.

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