Interaction of Bivalent Metal Ions with Maltol in Presence of Dicarboxylic Acids

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Factors contributing to the stability of the ternary complexes of the type MAL [where A = Maltol ; A = various polycarboxylic acids and M=Cu(II), Co(II), Ni(II), Zn(II)] have been studied potentiometrically.

Mixed ligand complexes have been studied extensively due to their biological importance [1-3]. In continuation to our earlier work [4,5] on ternary metal complexes of γ - pyrones, the formation constants of ternary complexes [MAL] [M=Co(II), Ni(II), Cu(II), Zn(II); A = maltol (3-hydroxy-2-methyl pyran-4-one) (MA); L = dicarboxylic acids (viz., Oxalic acid (Ox), Malonic acid (Malo), Succinic acid (Succ), Glutaric acid (Glut), Adipic acid (Adip), Maleic acid (Male), Fumaric acid (Fuma), Iminodiacetic acid (IMDA), Hydroxyethyliminodiacetic acid (HIMDA), and Nitrilotriacetic acid (NTA)] have been determined potentiometrically, in aqueous medium at 30°C and I=0.1M KNO_3.

EXPERIMENTAL

Maltol was obtained from Fluka (Switzerland). Unsaturated dicarboxylic acids - Maleic acid, Furmaric acid - were obtained from BDH - E. Merck. The ligands IMDA, NTA were from Sigma and HIMDA was from Fluka (Switzerland). The metal salts of Co(II), Ni(II), Cu(II), and Zn(II) were of AnalaR grade; the metal ion solutions were standardized volumetrically by titration with sodium salt of EDTA [6].

Acid dissociation constants of free ligands and formation constants (binary and ternary) of metal complexes were determined potentiometrically, measuring the pH of the solution containing ligands in absence or in presence of metal ions in 1:1 or 1:1:1 ratio, using a Control Dynamics pH meter fitted with a Gel filled electrode. The calculations were done using the experimental data based on the trends in the titration curves on a CASIO-PB-110 personal computer with the aid of suitable material balance equations.

RESULTS AND DISCUSSION

An inflection (steep or feeble) is observed at m=2 followed by another inflection at m=3, in the potentiometric curves for 1:1:1 ternary system involving M(II), maltol and dicarboxylic acids (*viz.*, Ox, Malo, Succ, Glut,

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Adip, Male, Fuma, IMDA HIMDA). The inflection suggests the formation of ternary complexes in step wise manner, in which MA binds only after the complete formation of binary 1:1 metal - dicarboxylic acid complexes. The following equations have been derived from the graphs:

$$M(II) + AH_2 \rightleftharpoons [MA] + 2H^+ \quad \ldots (1)$$

$$[MA] + HL \rightleftharpoons [MAL]^- + H^+ \quad \ldots (2)$$

But in the case of ternary complexes involving NTA, the first inflection is observed at m=3 and second at m=4 suggesting the following equilibria

$$M(II) + AH_3 \rightleftharpoons [MA]^- + 3H^+ \quad \ldots (3)$$

$$[MA]^- + HL \rightleftharpoons [MA]^{2-} + H^+ \quad \ldots (4)$$

The stability constants for the ternary complexes are given in Table 1 and their corresponding Δlog K along with %R.S. are given in Table 2.

The Δlog K values are found to be usually negative and are often the same as expected statistically in the absence of electrostatic effects [7] or of any specific interactions between the two ligands [8]. The expected statistical factor for these systems, assuming all the metal ions are in octahedral geometry, would be -0.4. If the observed Δlog K values are more negative than -0.4, then it is concluded that apart from statistical reasons, there are also some other factors responsible for destablisation.

Dicarboxylic Acids

The stability order with respect to primary ligands in the ternary complexes is Malo

Table 1

Log K^{MA}_{MAL} of Ternary Complex with Bivalent Metals

Maltol (L) as Secondary Ligand in presence of Different Dicarboxylic acids
pK_a of Maltol (MA) = 8.55 Medium Aqueous: I = 0.1 M KNO_3; T = 30°C

System	Co(II)	Ni(II)	Cu(II)	Zn(II)
log K^M_{ML}	5.35	5.57	7.61	5.77
OXalic acid + MA	4.78±0.05	4.89±0.03	6.07±0.07	5.20±0.04
Malonic acid + MA	5.01±0.02	5.15±0.03	6.30±0.06	5.32±0.08
Succinic acid + MA	4.67±0.05	4.85±0.08	5.97±0.09	5.08±0.03
Glutamic acid + MA	4.55±0.08	4.72±0.01	5.92±0.09	4.95±0.08
Adipic acid + MA	4.42±0.07	4.66±0.08	5.81±0.12	4.79±0.05
Maleic acid + MA	4.60±0.02	4.88±0.05	5.78±0.03	5.16±0.05
Fumeric acid + MA	4.52±0.05	4.82±0.07	5.70±0.08	5.06±0.01
IMDA + MA	3.65±0.01	3.84±0.04	5.80±0.02	4.25±0.02
HIMDA + MA	3.60±0.07	3.74±0.05	5.50±0.07	3.97±0.08
NTA + MA	3.39±0.05	3.39±0.01	3.12±0.08	3.72±0.06

Table 2

Comparison of Stability of Binary & Ternary Complexes for addition of Maltol (Δlog K & % R.S. Values)

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

System	Δlog K				% R.S.			
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
OXalic acid + MA	-0.57	-0.68	-1.54	-0.57	-10.65	-12.21	-20.23	- 9.87
Malonic acid +MA	-0.34	-0.42	-1.31	-0.45	- 6.35	- 7.54	-17.21	- 7.79
Succinic acid +MA	-0.68	-0.72	-1.64	-0.69	-12.71	-12.92	-21.55	-11.95
Glutamic acid+MA	-0.80	-0.85	-1.69	-0.82	-14.95	-15.26	-22.21	-14.21
Adipic acid + MA	-0.93	-0.91	-1.80	-0.98	-17.38	-16.33	-23.65	-16.98
Maleic acid + MA	-0.75	-0.69	-1.83	-0.61	-14.01	-12.38	-24.04	-10.57
Fumeric acid +MA	-0.83	-0.75	-1.91	-0.71	-15.51	-13.46	-25.09	-12.30
IMDA + MA	-1.70	-1.73	-1.81	-1.52	-31.77	-31.05	-23.78	-26.34
HIMDA + MA	-1.75	-1.83	-2.11	-1.80	-32.71	-32.85	-27.72	-31.19
NTA + MA	-1.96	-2.18	-2.49	-2.05	-36.13	-39.13	-32.72	-25.52

$$\Delta \log K = \log K^{MA}_{MAL} \log K^{M}_{ML}$$

$$\% \text{ R.S.} = \frac{\log K^{MA}_{MAL} - \log K^{M}_{ML}}{\log K^{M}_{ML}} \times 100$$

> Ox > Succ > Glut > Adip. This trend is the same as found in their 1:1 binary complexes (M)II) - dicarboxylic acids]. The ligand maltol forms 5 membered ring with these metal ions in its binary complexes. Similarly dicarboxylic acids being bidentate ligands form rings of different sizes, in their binary complexes. The ligands in mixed ligand complexes (with maltol as a common ligand and one dicarboxylic acid as the other) form chelates of different sizes: 5+6 in Malo, 5+5 in Ox, 5+7 in Succ, 5+8 in Glut and 5+9 in Adip. The observed trend is in accordance with the above said rule. The most common and the most stable complexes of dicarboxylic acids are 5 or 6 membered chelates. Sigel [9,10] formulated a tentative rule for the order of mixed ligand formation constants in ternary complexes containing two chelate rings formed by two different ligands as (5+6) > (6+6) > (5+5). This may be because the strain involved in forming larger ring systems could be more.

Aminopolycarboxylic acids

The order of stability with respect to these primary ligands is found to be IMDA > HIMDA > NTA. The destabilisation factors in these systems are

i) Statistical reasons
ii) Electrostatic repulsion
iii) Steric hindrance in HIMDA
iv) Denticity of ligands (Tetradentate over Tridentate).

IMDA and HIMDA upon coordination with M(II) form binary neutral complexes where as NTA forms mono negative binary complexes. Therefore, more electrostatic repulsion is expected between mono negative maltol and [M-NTA]$^-$ than between mono negative maltol and neutral [M-IMDA] and [M-HIMDA] binary complexes. Higher stability of [Cu-IMDA-MA]$^-$ system than [Cu-HGIMDA-MA]$^-$ system may be due to steric hindrance caused by ß-hydroxyethyl group in HIMDA.

Maleic acid and Fumaric acid

The order of stability is Maleic acid > Fumaric acid. Higher stability of Maleic acid is due the presence of double bond in the ligand which increases the stability of the complex due to the exocyclic conjugation. The Fumaric acid due to its trans geometry may impart greater strain during chelate formation, so it forms less stable ternary complex. The destablisation resulted in these systems is due to the following factors :

I) Statistical reasons
II) Trans geometry of Fumaric acid which is incapable of strong bidentate mode of binding.

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