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Interaction of Copper with Imidazole in Presence of Dicarboxylic Acids

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The interaction of Cu(II) with imidazole in presence of dicarboxylic acids, aminopolycarboxylic acids, maleic and fumaric acids has been investigated by a potentiometric method. The ternary complexes of amino polycarboxylic acids have Δ log K values less negative than the ternary complexes involving dicarboxylic acids, maleic and furmaric acids, Probable explanations for these are provided.

INTRODUCTION

As an extension of previous work,[1–3] the present paper reports the interaction of Cu(II)-imidazole in presence of various ligands such as oxalic acid (ox), malonic acid (mal), succinic acid (suc), glutaric acid (glu), adipic acid (adi) (dicarboxylic acids), iminodiacetic acid (IMDA), hydroxyethyliminodiacetic acid (HIMDA), nitrilotriacetic acid (NTA), (aminopolycarboxylic acids), maleic and fumaric acids.

EXPERIMENTAL

The experimental method consisted of the potentiometric titration of each ligand with standard NaOH solution in the absence and presence of the metal ions being investigated. The ionic strength of the solution was maintained approximately constant in the course of the titration by the use of a medium containing 0.1 M KNO_3 and relatively low concentration of ligand and metal ion. The temperature was maintained constant at 25°C throughout the course of titration (thermostatically). The control dynamic pH meter was used to determine the change in pH. The electrode system was calibrated from data tabulated by Harned and Owen[4].

Potentiometric Titration

Titrations were carried out in a double-walled titration cell maintained at 25°C. For determination of the dissociation constants and stability constants for the various binary and ternary metal complexes, the following set of solutions (total volume = 50 ml) were titrated potentiometrically with 0.141 N NaOH.

(i) 0.001 M ligand A,
(ii) 0.001 M Ligand A + 0.001 M Cu(II),
(iii) 0.001 M Ligand A + 0.001 M Cu(II) + 0.001 M L

Titration of each set was carried out twice to check the reproducibility of the data. The pH meter readings were plotted against 'a' (moles of base added per mole of ligand) or 'm' (moles of base added per mole of metal ion).

Calculations

(i) *Dissociation constants:* The following expressions were used to calculate acid dissociation constants of the ligand under investigation.

$$K_a = \frac{[H^+](aT_L + [H^+] - [OH^-])}{T_L - (aT_L + [H^+] - [OH^-])}$$

$$K_{2a} = \frac{[H^+](a-1)T_L + [H^+] - [OH^-]}{T_L - (a-1)T_L + [H^+] - [OH^-]}$$

where a = moles of base added per mole of ligand and T_L = total concentration of the ligand species.

(ii) *Stability constants for binary 1 : 1 system:*

(a) The equilibrium involved in the formation of 1 : 1 metal complexes of ligands 'L' may be represented as

$$M + H_2L \rightleftharpoons ML + 2H^+$$

For the calculation of K^M_{ML} of 1 : 1 copper-A system, the K_a and K_{2a} values of all the ligands were considered.

$$K^M_{ML} = (T_L - X(L))/X \cdot [L]^2$$

where $X = [[H^+]^2/K_aK_{2a}] + [[H^+]/K_{2a}] + 1$

$$L = [(2-a)T_L - [H^+] + [OH^-]]/[2[H^+]^2/K_aK_{2a}] + [[H^+]/K_{2a}]$$

(b) For the calculation of copper-imidazole 1 : 1 stability constants the following equilibrium is considered.

$$HA^+ \rightleftharpoons A + H^+$$

$$M + A \rightleftharpoons MA$$

$$K^M_{MA} = T_M - [M]/[M][L]$$

$$[L] = \beta \cdot K_a/H^+;\ \beta = (1-a)T_L - H^+ + OH^-;\ [M] = [([H^+]/K_a) + 1][L]$$

(iii) *Stability constants for ternary 1 : 1 : 1 systems:* The stability constants of the 1 : 1 : 1 ternary complexes were calculated by considering that the 1 : 1 Cu–[L] complex is completely formed before the coordination of the imidazole takes place. This situation is represented by the equilibrium

$$ML + A \rightleftharpoons MLA$$

$$K^{ML}_{MLA} = \frac{[MLA]}{[ML][A]}$$

The calculation of K^{ML}_{MLA} are similar to the calculation of K^{M}_{MA} 1 : 1 Cu-imidazole system. All calculations were performed using the experimental data based on the trends in the titration curves on a CASIO-PB-110 personal computer.

RESULTS AND DISCUSSION

The stability of the various ternary metal complexes and corresponding binary metal complexes has been quantitatively compared in terms of the parameter $\Delta \log K$ which is expressed as

$$\Delta \log K = \log K^{ML}_{MLA} - \log K^{K}_{MA}$$

$\Delta \log K$ values reflect the ability of the imidazole to bind the various Cu(II)-dicarboxylic acids/aminopolycarboxylic acids, binary complexes relative to the aquo-cupric ion. The $\Delta \log K$ values for the various ternary complexes have been calculated and are listed in Table 1 along with binary and ternary constants for various systems. In order to obtain precise values of $\Delta \log K$ it is essential that the binary and ternary constants should refer to identical experimental conditions. Acid dissociation constants of all the ligands under investigation and their binary constants and some of ternary constants have been reported earlier in literature[5–9] under different experimental conditions. Hence these constants have been redetermined in this work at 25°C and $\mu = 0.1$ M (KNO_3). The data in Table 1 show that $\Delta \log K$ values are negative for all ternary systems investigated. Based on a purely statistical basis negative values of $\Delta \log K$ are expected since there are more coordinating sites on the aquo metal ion relative to the binary metal complex. For the coordination of a bidentate ligand [L] to a square-planar metal ion already bound to a bidentate ligand the statistically

TABLE 1

STABILITY CONSTANTS OF MIXED LIGAND COMPLEX OF Cu(II)-IMIDAZOLE IN PRESENCE OF DICARBOXYLIC ACIDS

[$\mu = 0.1$ M (KNO_3); Temp. = 25°C; aqueous medium]

Imidazole $pK_a = 7.01$; $\log K^{Cu}_{Cu\text{-imidazole}} = 4.31$

Ligand [L]	$\log K^{Cu}_{CuL}$ (1 : 1)	$\log K^{CuL}_{CuL\text{-imidazole}}$ (1 : 1 : 1)	$\Delta \log K$	% R.S.
Oxalic acid	4.22	3.78	–0.53	–12.29
Malonic acid	4.75	3.97	–0.34	–07.88
Succinic acid	3.20	3.69	–0.62	–14.38
Glutaric acid	3.10	3.67	–0.64	–14.85
Adipic acid	2.54	3.62	–0.69	–16.00
IMDA	9.76	4.10	–0.21	–04.87
HIMDA	10.51	4.06	–0.25	–05.80
NTA	13.50†	4.16	–0.15	–03.48
Maleic acid	4.02*	3.85	–0.46	–10.67
Fumaric acid	3.19*	3.70	–0.61	–14.15

*Values taken from reference 6. † Values taken from reference 11.

expected Δ log K value is –0.6. In the present study the statistical factor for the binding of a monodentate secondary ligand (imidazole) to a square planar cupric ion already bound to a bidentate ligand (except IMDA, HIMDA, NTA) would be 2/4 and Δ log K = –0.30. Statistical factor for [tridentate (IMDA, HIMDA) as primary ligand] monodentate secondary ligand in square-planar geometry could be 1/2; accordingly Δ log K = –0.30. Δ log K values which are more negative or positive represent destabilization or stabilization respectively. In the present study all the ternary systems investigated exhibit Δ log K values more negative or less negative than the expected value (–0.30) on statistical grounds alone.

Another parameter % relative stabilisation (% RS) has been made use to measure the relative ease of the formation of mixed ligand complexes which may be defined[10] as $\% \text{ RS} = [(\log K^{ML}_{MLA} - \log K^{M}_{MA})/\log K^{M}_{MA}] \times 100$.

Dicarboxylic acids

The data in Table 1 (Δ log K and % RS) show that the stability order with respect to the primary ligands in ternary complex is mal > ox > suc > glu > Adi. This is the same trend as found in 1 : 1 Cu-dicarboxylic acids in their binary complexes. The most common and the most stable chelates are 5 or 6 membered chelates. Malonic acid which forms six-membered ring is more stable than oxalic acid which forms 5-membered ring. The succinic acid, glutaric acid and adipic acid form seven, eight and nine-membered ring respectively which are less stable than 5 and 6-membered rings. This may be due to the fact that the strain involve in these systems could be more.

Aminopolycarboxylic acids

The order of stability with respect to primary ligands is found to be NTA > IMDA > HIMDA. This trend could be explained taking electrostatic attractions into consideration. IMDA and HIMDA upon coordination with Cu(II) form binary neutral complex whereas NTA form mono-negative binary complex. Therefore, more electrostatic attraction is expected between neutral imidazole and $[\text{CuNTA}]^-$ than between imidazole and [CuHIMDA] or [CuIMDA]. Higher stabilities of [Cu-IMDA-imidazole] system than [Cu-HIMDA-imidazole] system may be due to steric hindrance caused by β-hydroxyethyl group in HIMDA.

Maleic and fumaric acid

The order of stability is maleic acid > fumaric acid. Higher stability of maleic acid is due to the presence of double bond in the ligand which increases the stability of the complex due to exocyclic conjugation. The fumaric acid due to its *trans* geometry may impart greater strain during chelate formation; so it forms less stable ternary complex.

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