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Equilibrium Studies on Some Ternary Complexes of Cu(II) with 1,3-Diamino Propane as Primary Ligand and O-O Donor Atoms as Secondary Ligands and its Comparison with Binary Complexes

SANGITA SHARMA*, JAYSHREE N. PATEL, J.J. VORA and J.D. JOSHI†
Department of Chemistry, North Gujarat University, Patan-384 265, India

The formation constants of the mixed ligand complexes (CuAL) at 1 : 1 : 1 optimum molar concentration of metal as Cu(II); primary ligand, A = 1,3-diamino propane (1,3-DiaP) and O-O donor atoms as secondary ligand, L = salicylic acid, DL-malic acid, DL-mandelic acid, DL-lactic acid have been determined by modified form of Irving-Rossotti titration technique in aqueous media at constant ionic strength $\mu = 0.2$ M dm^{-3} at 30 ± 0.1°C. The difference between the stability of ternary complexes and the corresponding binary complexes has been expressed in terms of parameter $\Delta \log K_T$. The stabilities of the ternary complexes are explained in terms of π-basicities, structures of secondary ligand and ring size of chelate. $\Delta \log K_T$ values are negative which suggests favourable formation of ternary complexes. The variations of $\Delta \log K_T$ have been explained in terms of $M \rightarrow L$ π-interaction, size of the chelate ring and steric factors.

Key Words: Formation constant, Potentiometric studies, Copper(II), Ternary complexes, Steric factors.

INTRODUCTION

Zinc and copper which are used in higher concentration than any of the non-ferrous transition metals especially bound by the protein metallothionein in biological systems[1, 2]. In biological systems copper binding is distinct from zinc, with twelve sites per molecule *via* clusters of —SH groups[3, 4]. The unusual metal environments of metal thioneins have attracted the attention of bioinorganic chemists[5–7]. In view of this fact several ternary complexes of transition metals are well studied[7–12].

In the present work, the formation constants of mixed ligand system (MAL) where A = 1,3-diamino propane and L = salicylic acid, DL-malic acid, DL-mandelic acid and DL-lactic acid determined by modified form of Irving-Rossotti titration technique in aqueous media at 30 ± 0.1°C are reported[13, 14]. The order of stability of mixed ligand complexes is explained in terms of basicity and structure of primary ligand (A) and secondary ligand (L).

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†Department of Chemistry, S.P. University, Vallabh Vidyanagar, Gujarat-388 120, India.

EXPERIMENTAL

1,3-Diamino propane, salicylic acid, DL-malic acid, DL-mandelic acid and DL-lactic acid (AnalaR), sodium perchlorate (Fluka), perchloric acid (Baker, analyzed) were used. A stock solution of Cu(II) perchlorate solution was standardized by complexometric EDTA titrations[15]. Carbonate-free NaOH solution was standardized by reported method[16].

Conductivity water is used throughout the experimental work. Digital μ-361 pH-meter with readability ±0.01 with combined glass calomel electrode has been used for potentiometrically. Stoichiometrically 1 : 1 : 1 concentration of Cu, A and L is maintained in the solution. Five sets of the solutions were prepared containing (1) known amount of free $HClO_4$ (2) free $HClO_4$ + known amount of primary ligand (3) free $HClO_4$ + known amount of primary ligand + known amount of metal perchlorate (4) free $HClO_4$ + known amount of secondary ligand (5) free $HClO_4$ + known amount of primary ligand + known amount of secondary ligand + known amount of metal perchlorate.

Total volume of each mixture was raised to 50 mL using conductivity water.

TABLE-1
MIXED LIGAND FORMATION CONSTANTS OF Cu(II)-HETEROCHELATES AT TEMPERATURE 30 ± 0.1°C, $\mu = 0.2$ M($NaClO_4$)

Ligand	pK_1^H	pK_2^H	pK_3^H	$\log K_{Cu\cdot L}^{Cu*}$	$\log K_{Cu\cdot L_2}^{Cu\cdot L*}$	$\log K_{Cu\cdot A\cdot L}^{Cu\cdot A}$	$\Delta \log K_T$
Salicylic acid	11.44	2.93	—	10.6	5.85	6.93	–3.67
DL-Malic acid	11.27	5.34	3.38	8.13	3.59	7.08	–1.05
DL-Mandelic acid	11.60	3.37	—	—	—	6.93	—
DL-Lactic acid	11.41	3.83	—	7.86	4.84	6.86	–1.00

*Values are taken from the literature:

$$\Delta \log K_T = \log K_{Cu\cdot A\cdot L}^{Cu\cdot A} - \log K_{Cu\cdot L}^{Cu}$$

where: A = 1,3-Diamino propane; L = O-O donor atoms

RESULTS AND DISCUSSION

From titration data given in Fig. 1, $\bar{n}H$, $\bar{n}$, pL, $pL - \log(1 - \bar{n}/\bar{n})$ were calculated on the basis of literature method[14, 17] and binary and ternary formation constants are presented in Table-1.

The stability constants of the ternary complexes can be determined using two approaches:

(1) Formation of [Cu·A·L] takes place in two steps

(a) $Cu^{2+} + A \rightarrow [Cu\cdot A]^{2+}$ and

(b) $[Cu\cdot A]^{2+} + L \rightleftharpoons [Cu\cdot A\cdot L]$; and

(2) Simultaneous reaction between the metal ion and two ligands resulting in the existence of various species namely AH^+, A, LH_2^+, LH, L^-, $[CuAL_2]$, $[CuAL]^+$, Cu^{2+}, $[CuA]^{2+}$, $[CuL]^+$, $[CuA_2]^{2+}$ and $[CuL_2]$[18]. (Herein the charges on

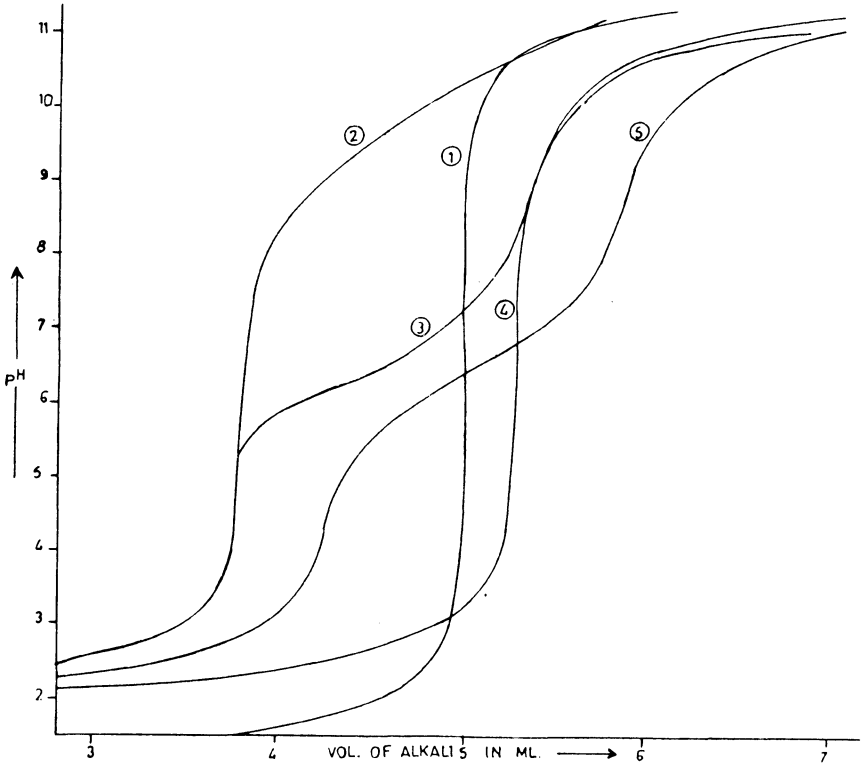

Fig. 1. Cu(II)-1,3-Diaminopropane salicylic acid system temp. 30 ± 0.1°C. (1) Acid, (2) 1,3-Diamono propane, (3) 1 : 1 molar ratio of Cu(II)-1,3-diamino propane, (4) Salicylic acid, (5) 1 : 1 : 1 molar ratio of Cu(II)-1,3-diamino propane salicylic acid

the species are omitted for convenience.) The $\Delta \log K^{MA}_{MAL}$ values obtained by the two methods agree well indicating that the formation of [CuA] is almost complete before the pH where it starts combining with secondary ligands O-O donor atoms. The mixed ligand formation constants of $\Delta \log K^{CuA}_{CuAL}$ are in the following order.

DL-Malic acid > Salicylic acid ≈ DL-Mandelic acid > DL-Lactic acid

The order is explained in accordance with the basicities of the ligands and structures of hydroxy acids. There is N → M σ-bonding; there exists M → N π-interaction due to back donating tendency. As a result of M—N bond the concentration of electrons around the metal ion in $M(1,3\text{-DiaP})]^{2+}$ does not increase significantly and electronegativing of metal ions in $M(1,3\text{-DiaP})]^{2+}$ remains same as $[M(H_2O)_n]^{2+}$. In the present study DL-malic acid has highest value of $\Delta \log K^{CuA}_{CuAL}$ because DL-malic acid is a tridentate ligand; the dissociation of first —COOH group brings inductive effect which reduces the dissociaton of second —COOH or —OH group and makes it more ligating.

Salicylic acid, DL-malic acid, DL-mandelic acid and DL-lactic acid are all bidentate in nature. Salicylic acid and DL-mandelic acid form more stable complexes than DL-lactic acid. The reason may be due to having benzene ring in their structure. Salicylic acid forms six membered chelates and DL-mandelic acid forms five-membered chelates; so salicylic acid should form more stable complexes than DL-mandelic acid although pK_1^H value for DL-mandelic acid is higher than salicylic acid. In salicylic acid, $\Delta \log K^{Cu \cdot A}_{Cu \cdot A \cdot L}$, the values for ternary complex are equal to DL-mandelic acid. The steric hindrance due to structure and approach towards $[Cu(II)\text{-}1,3\text{-}DiaP]^{2+}$ complex may be another cause for lowering the value of DL-mandelic acid and making it equal to salicylic acid. DL-lactic acid is monocarboxylic hydroxy acid and the inductive effect of —CH_3 groups makes lactic acid less acidic in comparison to other hydroxy acids.

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