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Effect of Excess of Secondary Ligand on Speciation and Stability in Some Ternary Complexes

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Stability constants of ternary complexes of type MAL where M = Ni(II) and Cu(II) and A = diamine (ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, *o*-, *m*- or *p*-phenylenediamine) and L = salicylic acid, have been determined by potentiometric method in aqueous medium at 30 ± 0.1°C at 0.2 M ionic strength under nitrogen atmosphere. Ratio of metal to primary ligand and secondary ligand is maintained at 1 : 1 : 1.5, 1 : 1 : 2 and 1 : 1 : 2.5 and compared. Stability of ternary complexes affected by concentration of secondary ligand along with other parameters like $\Delta \log K_T$, structure and basicity of primary and secondary ligand, steric factors, chelation, etc. Species distribution diagrams also reflect the effect of concentration of secondary ligand on percentage distribution of various species. FORTRAN-IV Program has been used for calculation and for pruning species like MAL, MAL_2, MA_2L, MAL_2H_2 etc., in equilibrium conditions.

Key Words: Stability constants, Secondary ligand, Ternary complexes.

INTRODUCTION

The role of metal ions indicates the importance of ternary chelates in the activation of enzymes in biological processes[1]. The possibility of formation of ternary complex in biological ligands makes it worth while to measure the stability of ternary complexes. There are a large number of potential ligands likely to compete with ions formed *in vio*[2]. A number of ternary systems are reported where metal, primary ligand and secondary ligand ratio is 1 : 1 : 1 maintained[3–5]. But a little is found in the literature about the behaviour of ternary complexes when concentration of secondary ligand changes and is in excess.

So, the present paper reports ternary complexes of Cu(II) and Ni(II) where A = ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, *o*-, *m*- or *p*-phenylenediamine. The ratio of M, A and L is maintained at 1 : 1 : 1.5, 1 : 1 : 2 and 1 : 1 : 2.5. The values of stability constants are compared with

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reported values[7-8] of the system where M, A and L ratio was maintained at 1 : 1 : 1. Besides other factors[9], the stability of ternary complexes is also governed by concentration of secondary ligand.

EXPERIMENTAL

All the diamines used were of AR grade and other reagents used are sodium perchlorate (Fluka), perchloric acid (Baker Analyzed), sodium hydroxide (BDH AnalaR grade). A stock solution of Cu(II) and Ni(II) perchlorate was prepared. Acid and metal contents of solutions under analysis were determined by acid-base[10] and complexometeric titrations[11]. All the stock solutions were prepared in conductivity water.

Potentiometric Titration Procedure: Determination of stability constants of ternary type 1 : 1 : 2.5 systems involved potentiometeric titration of a series of solutions of 12.5 mL 0.02 M of ligand containing 5 mL 0.2 M of free perchloric acid in absence and in presence of 5 mL 0.02 M metal ion with 0.2 M standard sodium hydroxide solution. Total volume of each set was raised to 50 mL and ionic strength was maintained 0.2 M using 1 M sodium perchlorate. Free ion contamination in studied solution was determined by Gran's plot[12]. Potentiometric titrations were performed in jacked glass reaction vessel in oxygen free atmosphere so as to avoid any side reactions[13].

Systronics 361 μ-pH-meter with combined glass and calomel assembly with a readability ±0.01 and temperature probe was used for potentiometric studies. μ-pH-meter was calibrated with buffer solution and calibration was checked intermittently.

Ratio of metal to primary ligand and to secondary ligand was maintained at 1 : 1 : 1.5, 1 : 1 : 2, 1 : 1 : 2.5 in different sets so prepared. All measurements were made in aqueous medium at temperature 30 ± 0.1°C at ionic strength 0.2 M (NaOH). The stability constants were calculated by method of weighted least square[14].

RESULTS AND DISCUSSION

The formation of ternary complexes can be represented as

$$[\text{M(diam.)}] + \text{L} \rightleftharpoons [\text{M-diam. L}]$$

$$K^{\text{M-diam.}}_{\text{M-diam. L}} = \frac{[\text{M-diam. L}]}{[\text{M-diam.}][\text{L}]}$$

The stability constants for ternary complexes were calculated considering that 1 : 1 $[\text{M(II)-diam.}]^{2+}$ is completely formed before coordination of secondary ligand takes place. The formation of [M-diam. L] complex is expected to take place by the following mechanism:

Ionization constant of protonated diamines and hydroxy acid can be represented as

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \qquad K^{\text{H}}_{\text{A}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{HL} \rightleftharpoons \text{H}^+ + \text{B}^- \qquad K^{\text{H}}_{\text{B}} = \frac{[\text{H}^+][\text{L}^-]}{[\text{HL}]}$$

$$\mathrm{HA + HL \rightleftharpoons 2H^+ + A^- + L^-} \qquad K_{AL}^{H} = \frac{[H^+]^2[A^-][L^-]}{[HA][HL]}$$

$$\mathrm{HAL \rightleftharpoons H^+ + AL^-} \qquad K_{AL}^{H} = \frac{[H^+][AL^-]}{HAL}$$

If [HA] and [HL] are same of quantity then binary equilibrium constants can be represented as

$$\mathrm{M + A \rightleftharpoons \underset{1:1}{MA}} \qquad K_{A}^{M} = \frac{[MA]}{[M][A]}$$

$$\mathrm{MA + A \rightleftharpoons \underset{\text{(Least possible)}}{\underset{1:2}{MA_2}}} \qquad K_{MA}^{M} = \frac{[MA_2]}{[MA][A]}$$

$$\mathrm{M + L \rightleftharpoons \underset{1:1}{ML}} \qquad K_{L}^{M} = \frac{[ML]}{[M][L]}$$

If concentration of L is in excess,

$$\mathrm{ML + L \rightleftharpoons \underset{\text{(Possible)}}{\underset{1:2}{ML_2}}} \qquad K_{ML}^{M} = \frac{[ML_2]}{[M][L]}$$

Now stability constant for ternary complexes is represented as

$$\mathrm{MA + L \rightleftharpoons MAL} \qquad K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]}$$

where A is primary ligand and L is secondary ligand.

The difference in stability, $\Delta \log K_T$, between the binary and ternary complexes is one way to characterize tendency towards the formation of ternary complexes[15].

$\Delta \log K_T$ values are negative because $\log K_{ML}^{M} > \log K_{MAL}^{MA}$, as more coordination positions are available for binding primary ligand to give multivalent metal ion than for secondary ligand. Various stability constants for ternary complexes are presented in Table-1.

Various simultaneous reactions between metal ions and ligands A and L result in formation of various species like AH_2, AH, LH_2, LH, CuA, CuA_2, CuL, CuL_2, CuA_2LH_2, $CuAL_2H_2$, CuAL, $CuAL_2$, $CuALH_{-1}$ (here charges on species are omitted for convenience). The species are calculated for different metal to ligand ratios (A and L) by assuming best fit chemical model of computer program. The species distribution graphs obtained in presence of excess of secondary ligand, *i.e.*, 1 : 2 : 2.5 are compared with 1 : 1 : 1 systems[6, 7].

Species distribution curves show that with increase in concentration of secondary ligand percentage of CuL_2, CuL and $CuAL_2$ increases considerably in all ternary systems and percentage decreases in CuAL indicating that formation of CuAL type of complexes is maximum when 1 : 1 : 1 ratio of metal, primary ligand and secondary ligand is considered. There is a striking difference in the species distribution of ternary systems of Cu(II) and Ni(II); also in molar ratio of 1 : 2 : 2.5 as compared to 1 : 1 : 1. The MAL are found to be accounting maximum of *ca.* 50% of total of metal ion or ligand A or ligand L at pH 7.8 whereas it has been favoured at *ca.* 48% at pH 6.3 in case of Cu(II) ternary systems. Because of the preferred structural characteristics of NiL_2 binary species[16], these species are somewhat predominant in 1 : 1 : 2.5 solution in ternary systems. The formation of $NiABH_{-1}$ species occurs at pH 6 and $CuABH_{-1}$ occurs at pH 6.4. Its concentration goes on increasing with addition of alkali volumes. As expected, $NiAL_2$ species have been favoured in 1 : 1 : 2.5 solution and reaches to maximum value of *ca.* 30% but $CuAL_2$ species reaches to maximum value of *ca.* 10% in 1 : 1 : 2.5 solution. In order to demonstrate this quantitative trend, the species distribution plots in 1 : 1 : 1 and 1 : 1 : 2.5 solutions of Cu(II) are presented in Fig. 1.

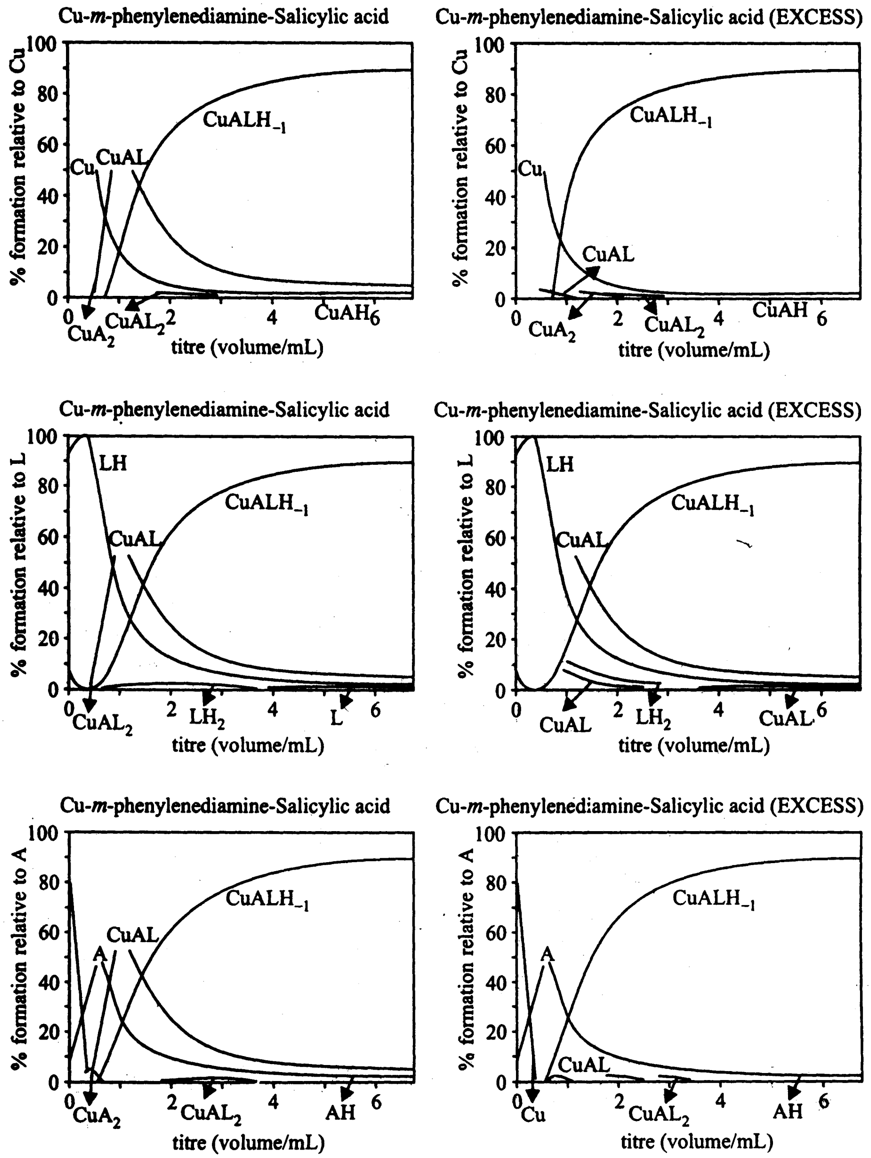

Fig. 1. Species Distribution Diagrams for CuAL in molar ratio of 1 : 1 : 1 and 1 : 1 : 2.5

TABLE-1
FORMATION CONSTANTS OF SOME TERNARY COMPLEXES OF Cu(II) AND Ni(II) AT 30 ± 0.1°C, IONIC STRENGTH $\mu = 0.2$ M dm^{-3} (NaOH)

Complexes	Molar ratio of M, A, L			
	1 : 1 : 1	1 : 1 : 1.5	1 : 1 : 2	1 : 1 : 2.5
Ni-en-Sal.	6.38	6.32	6.30	6.27
Ni-1,2 dap-Sal.	6.48	6.30	6.10	5.98
Ni-1,3 dap-Sal.	6.43	6.28	6.07	5.97
Ni-opda-Sal.	7.03	6.90	6.79	6.68
Ni-mpda-Sal.	6.82	6.40	6.10	5.83
Ni-ppda-Sal.	7.12	7.07	6.99	6.94
Cu-en-Sal.	8.85	8.61	8.42	8.24
Cu-1,2-dap-Sal.	8.17	8.15	8.11	8.08
Cu-1,3-dap-Sal.	7.87	7.61	7.50	7.39
Cu-opda-Sal.	9.27	9.05	8.92	8.86
Cu-mpda-Sal.	9.38	8.50	8.21	8.01
Cu-ppda-Sal.	9.39	9.10	8.91	8.77

where en = ethylene diamine, 1,2 dap = 1,2 diaminopropane, 1,3 dap = 1,3 diaminopropane, opda = *o*-phenylenediamine, mpda = *m*-phenylenediamine, ppda = *p*-phenylenediamine.

Stability of ternary complexes is governed by basicity and structure of primary and secondary ligand, ring formation, $\Delta \log K_T$ value, steric factors and concentration of secondary ligand. The stability constant values are lower when secondary ligand is used which creates unfavourable environment for the formation of MAL and may favour ML_2 or MAL_2. Moreover, stability constant values are lower but are not drastically reduced as reported earlier[17]. Diamines are strong bases and therefore electron donating capacity is more. Excess of secondary ligand which is hydroxy acid may not be able to reduce acidity of metal ion which is surrounded by secondary ligand (L). Moreover, $\log K_{MAL}^{MA}$ values for aromatic diamines are higher than those for aliphatic diamines when used as primary ligands. Ternary complex formation is more favoured than binary complexes because stability complexes of diamines are higher than that of corresponding hydroxy acid.

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