

STUDY OF FORMATION CONSTANTS AND MECHANISM OF TERNARY COMPLEXES OF Ni (II) WITH DIAMINE AS PRIMARY LIGAND AND HYDROXY ACID AS SECONDARY LIGAND

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ABSTRACT

The formation constants for the ternary complexes of the type NiAL where A = ethylenediamine or 1, 2–diaminopropane or 1,3–diaminopropane or o–phenylenediamine or m–phenylenediamine or p–phenylenediamine and L = salicylic acid have been determined pH metrically at 30°C and $\mu = 0.2 \text{ M dm}^{-3}$ (NaClO₄). The values of formation constants are in the order of p–phenylenediamine > o–phenylenediamine > m–phenylenediamine > 1,2–diaminopropane > 1,3–diaminopropane > ethylenediamine. This order is explained in terms of basicity of primary and secondary ligand, structure of ligands, size of chelates ring, steric hindrance and $\Delta \log K_T$, values.

Key words : Ternary complex, Diamine, Salicylic acid, Formation constant.

INTRODUCTION

The ever increasing importance of ternary complexes especially those involving ligands containing functional groups identical with those present in enzymes viz. –COOH, –NH₂, –CONH, etc. is obvious from the application of such complexes in many analytical and biological reactions^{1–5}. Nickel activates many enzymes like arginase, tyrosinase, phosphoglucomutase etc. and stabilizes RNA and DNA against thermal denaturation⁶. α –Hydroxy acid is used in cosmetic industry in skin care products⁷. This prompted us to carry out this type of study for Ni (II) – diamine–salicylic acid ternary complex systems.

In present communication, ternary formation constants of type $\log K_{\text{NiAL}}^{\text{NiA}}$ are reported, where A = Diamines (ethylenediamine or 1,2–diaminopropane or 1,3–diaminopropane or o–phenylenediamine or m–phenylenediamine or p–phenylenediamine) and L = Salicylic acid.

EXPERIMENTAL

All diamines (ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine) are Anal R grade, sodium perchlorate (Fluka), Salicylic acid (Anal R), perchloric acid (Baker analysed) and sodium hydroxide (Anal R) were used.

A stock solution of $\text{Ni}(\text{ClO}_4)_2$ was prepared and standardised with EDTA solution⁸. Carbonate free standard sodium hydroxide solution⁹ was used for carrying out titrations. Digital μ pH-meter Systronic-361 with readability ± 0.01 was used for pH metric measurements. Modified form of Irving-Rossotti titration technique have been used^{10,11}.

The following five sets were prepared for titrations

- (1) Known amount of HClO_4
- (2) Free HClO_4 + Known amount of primary ligand
- (3) Free HClO_4 + Known amount of secondary ligand
- (4) Free HClO_4 + Known amount of primary ligand + Known amount of metal perchlorate.
- (5) Free HClO_4 + Known amount of primary ligand + Known amount of secondary ligand + Known amount of metal perchlorate.

The 1:1:1 molar ratio of Ni, A and L was maintained in the solution and the ionic strength of each solution is raised to 0.2 M dm^{-3} using sodium perchlorate and total volume was kept 50 mL.

Titration plots are presented in Fig. 1. From titration data, \bar{n}_H , \bar{n} and pL were calculated using equations given earlier¹⁰. More precise values of formation constants for ternary complexes were calculated by the method of linear plots¹² and values are presented in Table 1.

Table 1. Dissociation constant of free ligands and formation constants of Ni (II)-diamine-salicylic acid complexes at temperature = $30^\circ\text{C} \pm 0.1^\circ\text{C}$ and ionic strength = 0.2 M dm^{-3} (NaClO_4)

Primary Ligand (A)	pK _{1H}	pK _{2H}	$\log \frac{K_{\text{NIA}}}{K_{\text{NIAL}}}$	$\Delta \log k_T$
Ethylenediamine	9.85	6.94	6.38	-0.57
1,2-Diaminopropane	10.04	6.65	6.48	-0.47
1,3-Diaminopropane	10.90	8.85	6.43	-0.52
o-Phenylenediamine	4.61	1.81	7.03	+0.08
m-Phenylenediamine	5.01	2.56	6.83	-0.012
p-Phenylenediamine	6.22	2.99	7.12	+0.17

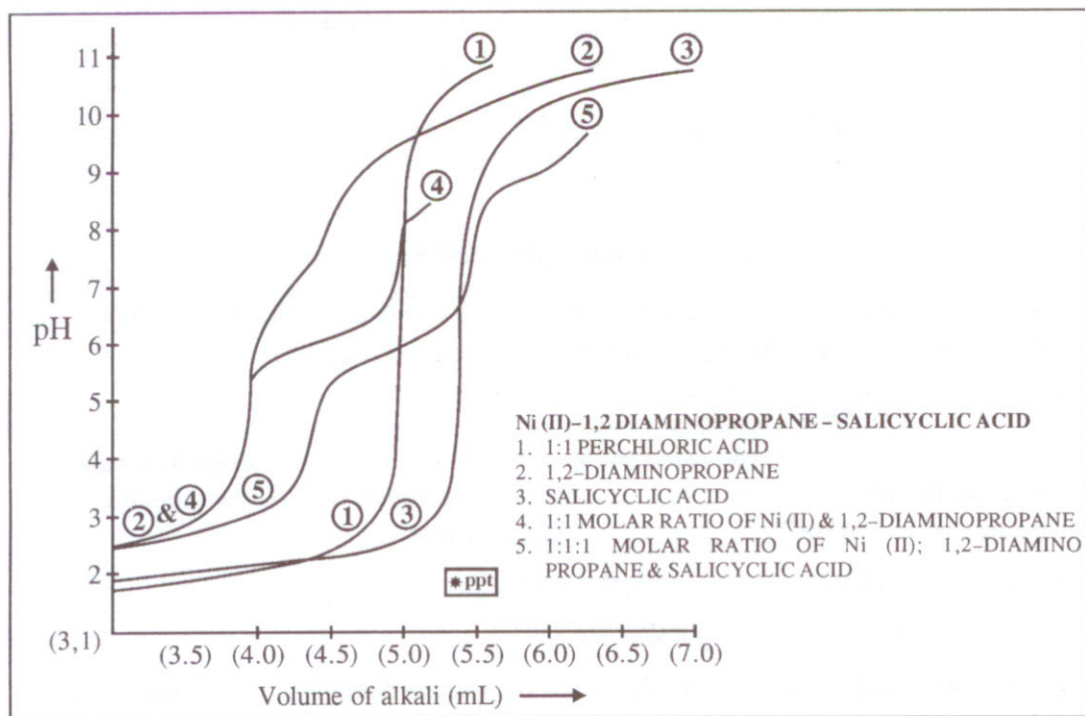
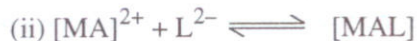


Figure 1. Ni (II) – 1, 2–diaminopropane–salicylic acid system

RESULTS AND DISCUSSION

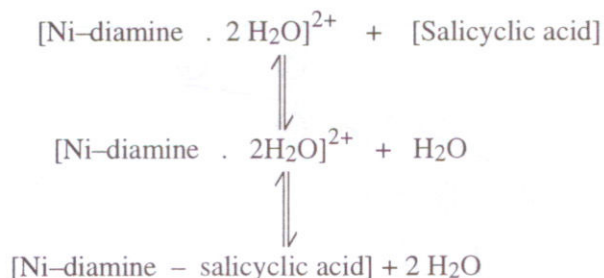
The formation of ternary complex is represented as follows



$$\text{Formation constant } K_{MAL}^{MA} = \frac{[MAL]}{[MA]^{2+} [L]^{2-}}$$

Where M = Ni and A = Ethylenediamine or 1,2–diaminopropane or 1,3–diaminopropane or o–phenylenediamine or m–phenylenediamine or p–phenylenediamine and L = Salicylic acid.

The formation constants of 1:1:1 ternary complexes for Ni (II)–diamine–salicylic acid were calculated, considering that 1:1 [Ni (II)–diamine]²⁺ is completely formed¹³ before coordination of secondary ligand takes place. The formation of Ni (II)–diamine–salicylic acid is expected to take place by following mechanism.



The relative stabilities of the ternary complexes are compared with corresponding binary complexes and it can be quantitatively expressed in terms of $\Delta \log K_T$ ¹⁴.

$$\Delta \log k_T = \log k_{\text{NiAL}}^{\text{NiA}} - \log k_{\text{NiL}}^{\text{Ni}}$$

The $\Delta \log k_T$ values are negative indicating stability of complexes. Also positive values for $\Delta \log k_T$ indicate enhanced binding of L as a result of the effects of A on the properties of the metal centre and vice versa¹⁴.

L = Salicylic acid, $\text{p}K_1\text{H} = 12.38$, $\text{p}K_2\text{H} = 2.98$,

$$\log k_{\text{NiL}}^{\text{Ni}} = 6.95, \quad \log k_{\text{NiL}_2}^{\text{Ni}} = 4.80$$

The proton ligand formation constant values for various diamines used as primary ligand are in the following order as per the reported values^{15,16}.

1,3-diaminopropane > 1,2-diaminopropane > ethylenediamine > p-phenylenediamine > m-phenylenediamine > o-phenylenediamine.

The formation constants of ternary complexes $\log k_{\text{NiAL}}^{\text{NiA}}$ are in following order –

p-phenylenediamine > o-phenylenediamine > m-phenylenediamine > 1,2-diaminopropane > 1,3-diaminopropane > ethylenediamine.

This order can be explained in terms of basicity of primary and secondary ligand, structure of ligand, size of chelate ring and steric hindrance. Formation constant values for ternary complexes with aromatic diamines are higher than aliphatic diamines in the present study. The reason may be that aromatic diamine ternary complexes have delocalization of the π -electrons in the metal-chelate ring¹⁴. The $\log k_{\text{NiAL}}^{\text{NiA}}$ value is highest for Ni (II) p-phenylenediamine-salicylic acid in the selected group of diamines, although $\text{p}K_1\text{H}$ value is the highest for 1,3-diaminopropane. The proton ligand formation constant value for p-phenylenediamine is highest amongst the aromatic diamines selected. The formation constant value for o-Phenylenediamine ternary complex is higher than m-phenylenediamine ternary complex, although $\text{p}K_1\text{H}$ value of m-phenylenediamine is greater than o-phenylenediamine. m-phenylenediamine has less convenient situation for coordination as compared to o-phenylenediamine as per position of two amino groups present on aromatic ring¹⁷. The special

conformation of the ligands with nitrogen atoms in meta or para position on the aromatic rings facilitates the formation of dimer complexes since the ligand acts as a bridge¹⁶.

Among aliphatic diamines, the ternary complex of Ni (II)–ethylenediamine–salicylic acid has lowest value of $\log \log k_{\text{NiAL}}^{\text{NiA}}$ as expected. Ni (II)–1,2–diaminopropane–salicylic acid complex is more stable than Ni (II)–1,3–diaminopropane–salicylic acid and Ni (II)–ethylenediamine–salicylic acid complexes. The reason may be the that 1,3–diaminopropane forms a six membered chelate ring and 1,2–diaminopropane forms a five membered chelate ring with metal ion¹³ and in aliphatic chelate five membered ring is more stable than the six membered ring^{14,18}.

CONCLUSION

The ternary complexes of salicylic acid with Ni (II) are more stable in presence of aromatic diamine as primary ligand than the aliphatic diamine as primary ligand. Moreover, the process of complexation in nickel is governed by pK_1H values of ligands, steric factors, ring size of chelate and $\Delta \log k_T$ factor.

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