Int. J. Chem. Sci. : 3 (2), 2005, 295–300

Ni (II)–MERCAPTOSUCCINIC ACID / 2–MERCAPTOPROPIONYL GLYCINE –AMINO ACIDS TERNARY COMPLXES – A POTENTIOMETRIC STUDY

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ABSTRACT

Formation of ternary complexes of Ni (II) with mercaptosuccinic acid (MSA), 2–mercaptopropionyl glycine (2–MPG)(L_1) and amino acids (L_2) has been studied in aqueous medium at 26 ± 0.5°C and 0.1M ($NaClO_4$) ionic strength potentiometrically. The stabilities of the ternary complexes were quantitatively compared with the stabilities of corresponding amino acid–Ni (II) binary complexes in terms of parameter Δ log K.

Key words : Potentiometric, Nickel (II), 2–Mercaptosuccinic acid, 2–Mercaptopropionyl glycine

INTRODUCTION

Ternary complexes play an important role in various biological systems. The compounds bearing carboxylic, amino, and sulphydryl groups serve as versatile ligands to chelate toxic and nutrient metal ions in biological systems. They act as non–specific ligands towards metal ions in terestial and aquatic systems. A meagre work is reported[1,4] on systematic investigation of ternary complexes involving sulphur–containing ligands such as mercaptosuccinic acid (MSA) and 2–mercaptopropionyl glycine (2–MPG), with transition metal ion Ni (II). Nickel, though in traces, is one of the most essential elements for healthy human life. It has been found that nickel–containing protein occurs in blood serum of man and other mammals. Nickel activates many enzymes and stabilizes RNA and DNA against thermal denautration[5,6] and it is a constituent of the enzyme urease present in plant cell. There are at least five different nickel dependent enzymes known[7,8].

The aim of present investigation is to study the ternary complexes of the type Ni (II)–MSA–amino acids and Ni (II)–2–MPG–amino acids. The complex equilibria of sulphur containing ligands is determined by mercapto sulphur, which is soft in character[9] .The mercapto group of these ligands participates in both; redox and acid–base reactions[10].

EXPERIMENTAL

The ligands MSA, 2–MPG (Sigma), glycine (gly), alanine (ala), valine (val), cysteine (cys), and penicillamine (pen) (SD fine) were used without further purification. All the solutions were

prepared in double distilled water. The nickel solution was prepared by dissolving nickel nitrate (AR) in glass distilled water and standardized using EDTA[11] .The standard solution of sodium hydroxide (E Merck) was prepared[12] in carbonate free glass distilled water and standardized potentiometrically against potassium hydrogen phthalate. Sodium perchlorate and perchloric acid solutions were prepared by dissolving requisite amounts of AnalaR samples in double distilled water. Elico digital pH meter (model LI 120) and combined glass electrode (CL 51) having pH range 0–14 were used to measure pH at $26 \pm 0.5^{o}C$ in 0.1M ($NaClO_4$) ionic strength. All the experiments were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solution through out the course of titration.

The Calvin–Bjerrum's pH titration technique as modified by Irving and Rossotti[13] was applied to determine formation constants. In experimental procedure, following thermostated mixtures were titrated with carbonate free 0.21 M sodium hydroxide solution:

1. 2 mL of 0.24M $HClO_4$
2. 2 mL of 0.24M $HClO_4$ +10 mL of 0.01M ligand L_1
3. 2 mL of 0.24M $HClO_4$ +10 mL of 0.01M ligand L_1 + 2 mL of 0.01M Ni (II) solution
4. 2 mL of 0.24M $HClO_4$ +10 mL of 0.01M ligand L_2
5. 2 mL of 0.24M $HClO_4$ +10 mL of 0.01M ligand L_2 + 2 mL of 0.01M Ni (II) solution
6. 2 mL of 0.24M $HClO_4$ +10 mL of 0.01M ligand L_1 +10 mL of 0.01M ligand L_2 + 2 mL of 0.01M Ni (II) solution

The total volume of above solutions was made 50 mL and ionic strength was maintained to 0.1M with the help of $NaClO_4$. The titrations are presented in Fig.1.

RESULTS AND DISCUSSION

Mercptosuccinic acid contains an active – SH group, which is α to one – COOH group and β to another – COOH group. It has three replaceable protons. The first protonation constant is due to – SH group while second and third are due to two – COOH groups.

Fig.1 shows that the pH titration curves of amino acids lie before acid curve indicating that in acidic solution, each ligand molecule is in association with one equivalent proton. This proton should be attached to the lone pair of electrons present on amino group[14,15]. This corresponds to the two deprotonation steps of the protonated ligand as below –

$$HLH^{+} \rightleftharpoons {}^{+}HL^{-} + H^{+} \quad ...(1)$$

$${}^{+}HL^{-} \rightleftharpoons {}^{-}H^{+} + L^{-} \quad ...(2)$$

Equation (1) corresponds to ionization of – COOH group while equation (2) denotes the deprotonation of proton attached to nitrogen atom. The former takes place in the pH region 2.00

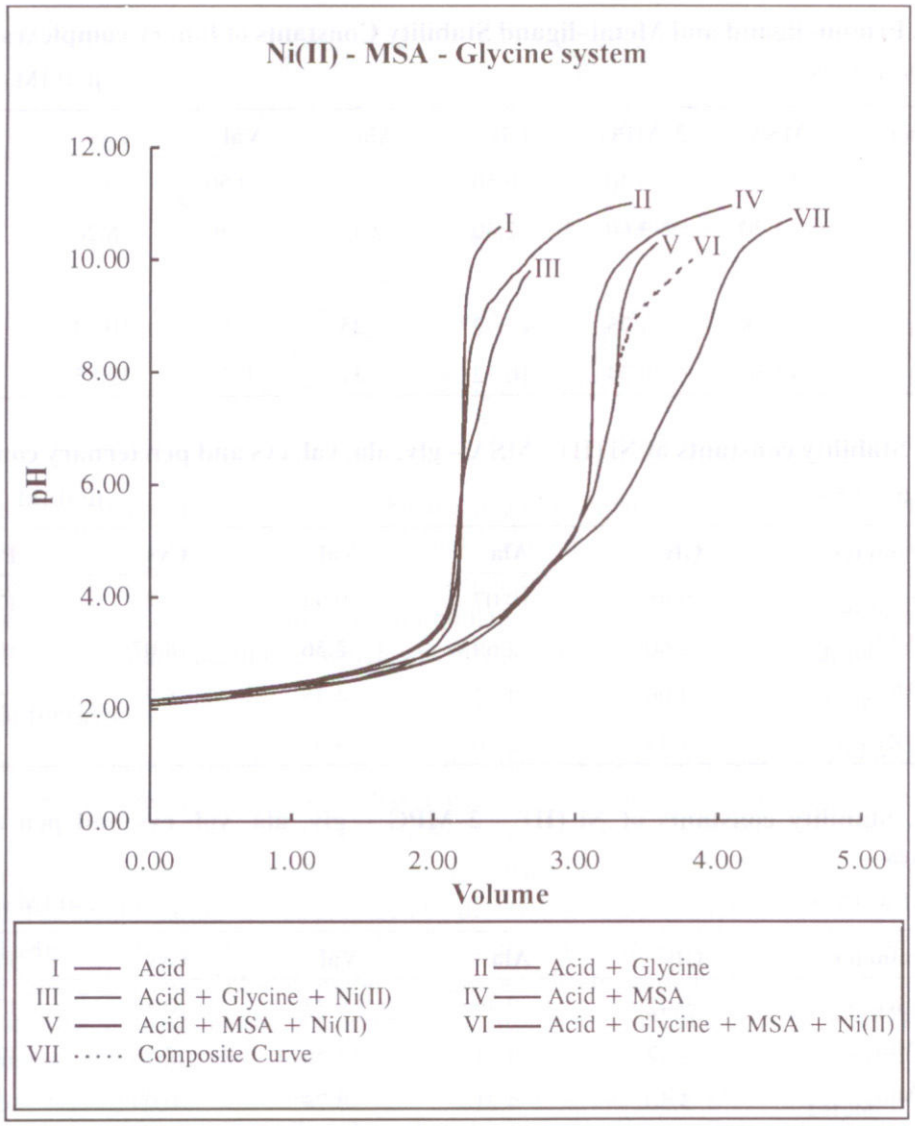

Fig 1. Potentiometric titration curves of Ni (II)–MSA–Glycine system

to 3.00 and later in pH range 6.50 to 11.00. Earlier reports also indicate similar step of deprotonation[16–22].

The proton–ligand and metal–ligand stability constants were determined by Irving and Rossotti method and values are presented in Table 1.The MSA and amino acids forms 1 : 1 and 1 : 2 complexes with Ni (II). MSA binds metal through –SH and α–COOH group. Gly, ala and val bind through –COOH and $–NH_2$ groups, while cys and pen bind metal through –SH and $–NH_2$ groups[23].

Table 1. Proton–ligand and Metal–ligand Stability Constants of binary complexes

Temp. =26 ± 0.5 °C μ=0.1M ($NaClO_4$)

Parameter	MSA	2–MPG	Gly	Ala	Val	Cys	Pen
$LogK^1_H$	10.50	8.40	9.56	9.63	9.50	10.40	10.50
$LogK^2_H$	4.70	3.60	2.40	2.40	2.36	8.20	7.80
$LogK^3_H$	3.20	—	—	—	—	—	—
$Log\beta_{ML1}$	7.38	4.75	5.92	5.25	5.59	10.24	11.88
$Log\beta_{ML2}$	13.30	9.34	10.72	9.31	9.38	19.85	22.30

Table 2. Stability constants of Ni (II) – MSA – gly, ala, val, cys and pen ternary complexes

Temp. =26 ± 0.5°C μ=0.1M ($NaClO_4$)

Parameter	Gly	Ala	Val	Cys	Pen
$Log\beta_{ML1L2}$	9.98	10.07	9.94	15.45	17.38
$LogK^{ML1}_{ML1L2}$	2.60	2.69	2.56	8.07	10.00
$LogK^{ML2}_{ML1L2}$	4.06	4.82	4.35	5.21	5.50
$\Delta LogK_{ML1L2}$	3.33	2.56	3.03	2.17	1.38

Table 3. Stability constants of Ni (II) – 2–MPG – gly, ala, val, cys and pen ternary complexes

Temp. =26 ± 0.5 °C μ=0.1M ($NaClO_4$)

Parameter	Gly	Ala	Val	Cys	Pen
$Log\beta_{ML1L2}$	9.42	9.46	9.33	10.33	17.55
$LogK^{ML1}_{ML1L2}$	4.67	4.71	4.58	5.58	12.16
$LogK^{ML2}_{ML1L2}$	3.50	4.21	3.74	0.09	5.67
$\Delta LogK_{ML1L2}$	1.25	0.54	1.01	4.66	–0.22

Stability constants of the ternary complexes namely Ni (II)–MSA/ 2–MPG– gly, ala, val, cys and pen are discussed in Tables 2 and 3. The Log K^{NiL2}_{NiL1L2} (=Log β_{NiL1L2} –Log K^{Ni}_{NiL1}) values obtained in the present systems (Table 2) compare favorably with log K_1 (Table 1). Hence it can be concluded that in ternary complex species also, MSA binds the metal ion in similar manner. Again Log K^{NiL1}_{NiL1L2} (=Log β_{NiL1L2}– Log K^{Ni}_{NiL1}) values obtained in ternary systems bear favorable comparison with the corresponding logK_1 values (Table 1) obtained in Ni–gly, ala, val, cys and pen systems after taking into account the statistical factors. This

demonstrates that in Ni L_1L_2 species nickel (II) ion binds in the same way as in its binary species. The glycine like binary mode results in five membered rings, which are very stable due to less strain. Thus Ni L_1L_2 species in all these mixed ligand complex systems would contain two five membered chelate ring. The values of ΔLog K_{NiL1L2} (=Log β_{NiL1L2} – Log β_{NiL1A} – Log $\beta_{NiL/1}$ obtained in these systems are compared to statistical values[24], which confirms that MSA/2–MPG and amino acid anion preferentially form ternary complexes over the binary ones and making extra stabilization of ternary complexes.

The formation of ternary complex is favored in the present investigation because the coordinating atoms on both sides of the metal ion are same and chelate rings on both sides are identical in size. The experimental values of ΔLog K lead to the conclusion of involvement of oxygen atom of carboxylic group of both amino acids and mercaptosuccinic acid /2–mercaptopropionylglycine.

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Prof. D. G. Dhuley for his kind guidance and to the University Grants Commission for the grant of Teacher Research Fellowship.

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Accepted : 2.3.2005