

ORIGINAL ARTICLE

STABILITY CONSTANT OF NICKEL(II) COMPLEX WITH AMINO ACID IN DIOXAN-
WATER MIXTURE

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ABSTRACT

A potentiometric titration technique has been used to determine the stability constants for the complex of Ni(II) with Glycine (A) as primary ligand and selected amino acids (L) as secondary ligands. Ternary complexes of amino acids are formed in a stepwise mechanism, whereby (A) binds to Ni(II), followed by interaction with ligand (L), whereas thiol-containing ligands form ternary complexes through a simultaneous mechanism. The formation constants of the complexes were determined at 35°C and ionic strength 0.1 M NaClO₄. The relative stabilities of the ternary complexes are compared with those of the corresponding binary complexes in terms of log K values. The concentration distribution of the complexes are evaluated.

.Keywords: MDPT, IR, Microanalyser, Glycine, Potentiometric technique

1.INTRODUCTION

Metal coordination complexes have been extensively used in clinical applications as enzyme inhibitors¹, anti-bacterial^{2,3}, antiviral⁴⁻⁶ and as anti-cancerous⁷⁻⁹. Different kinds of metals have been employed in these complexes including platinum, gold, vanadium, iron, molybdenum, cobalt, tin, gallium, copper and many others⁸. Metal complexes of adenine (A) have been shown to possess anticancer activity⁹⁻¹³. In living systems, almost all the biochemical processes are known to proceed mostly in the solution phase where several metal ions are present in trace quantities. Most of the physiological activities regarding nucleic acid interactions are promoted by metal ions through the formation of ternary (mixed-ligand) complexes¹⁴⁻²⁰. Whenever a metal ion exists in solution together with two or more different ligands, the formation of various simple as well as ternary (mixed-ligand) complexes is always possible, depending on the pH of the system. The actual complex-formation depends on the affinity of the metal ion towards the various ligands present, and the relative concentrations thereof. In the present study, the stability constants of mixed complexes from adenine and amino acids with Ni(II) were determined using potentiometric method. The concentration distribution relations of the various complex species will be evaluated.

2.MATERIALS AND METHODS

E. Merck sample of sodium hydroxide was dissolved in double distilled water in a Pyrex flask. The layer of carbon dioxide on the sodium hydroxide pellets was washed away previously. The solution was standardized potentiometrically against a standard oxalic acid solution. The stock solution of perchloric acid was prepared by diluting AR, BDH sample to required sample to required concentration and this was titrated potentiometrically against standard alkali solution. 1,4-Dioxan was purified by standard method²¹. An AR, BDH sample of sodium perchlorate was dissolved in double distilled water to make the stock solution of strength 1 mol dm⁻³.

Preparation of 3-methyl-2,6-diphenyl piperidin-4-thiocarbohydrazone

An equimolar (0.05 mol dm⁻³) mixture of 3-methyl-2,6-diphenylpiperidine-4-one²² and thiocarbohydrazone²² was treated with 1g of anhydrous sodium acetate in 150 ml of rectified spirit. This mixture was refluxed for 12 to 16 hrs. The insoluble product was filtered off and the volume of the filtrate was reduced by heating over a steam bath and poured into de-ionized water. The pale yellow colored product formed was filtered in a bucket funnel, dried and was recrystallized from benzene-petroleum ether (40-60°C) fraction. Yield was 40% (m.p.79°C). The purity of the product was checked by TLC method.

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Characterization of ligands

Microanalyser, UV and IR techniques characterized the ligand MDPT. IR spectra were recorded on a JASCO 700 spectrophotometer in KBr pellets and UV spectrum was recorded on a UVIDEC-340 spectrophotometer, using a quartz cell, 1 cm in dioxan medium.

Microanalysis of the ligand MDPT was determined by standard method nitrogen²³ and sulphur²³; Ni:19.40 (19.83), S: 9.00 (9.06), for MDPT.

Calibration of pH meter in dioxan-water medium

A mixture of 50% (v/v) dioxan-water medium was used since the chelates formed are relatively insoluble in water. Therefore, it was necessary to calibrate the pH meter in dioxan-water medium. To accomplish this the following concentrations of perchloric acid in 50% (v/v) dioxan-water medium were prepared (total volume 50 ml) and the pH meter readings (B values) were measured in all cases

3. RESULT AND DISCUSSION

The acid dissociation constants of the ligands and the formation constants of their binary complexes were previously reported²⁵. We have redetermined these constants under the prevailing experimental conditions as those utilized for determining the stability constants of the mixed-ligand complexes. The results obtained are in good agreement with the literature data²⁵.

Binary nickel(II) complex formation equilibria with Glycine

Glycine was titrated in the presence and absence of Ni(II) ion. The titration curve of the Ni(II) complex is lowered from that of the free glycine curve. This indicates a complex formation associated with release of hydrogen ions. The formation constants were determined by fitting potentiometric data on the basis of possible composition models. The selected model with the best statistical fit was found to consist of Ni(A) and Ni(A)H complexes.

The association constant of MDPT, glycine, and its stability constant of binary and ternary Ni(II) determined in 50% (v/v) 1-4-dioxane water mixture at 35°C and data are given in Tables (1-3) and Figs. (1).

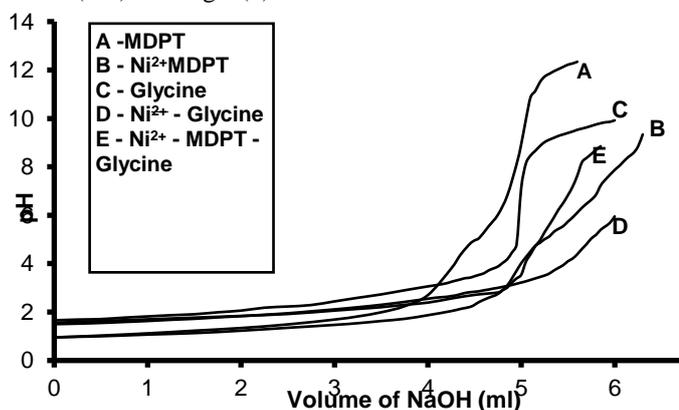


Fig. 1. pH metric titration curve for Ni²⁺ -MDPT - Glycine system

Table 1 pH titration data of Ni²⁺ with MDPT at 35 ± 0.1°C in dioxan-water (50% v/v)

Ionic strength [I] = 0.1 mol dm⁻³ [MDPT] = 0.00517 mol dm⁻³
[HClO₄] = 0.010442 mol dm⁻³ [Ni²⁺] = 0.0015 mol dm⁻³

Volume of NaOH ml	pH meter reading	
	MDPT	Ni ²⁺
0.00	0.95	0.96
0.50	1.03	1.00
1.0	1.12	1.07
1.50	1.23	1.13
2.00	1.34	1.23
2.50	1.49	1.35
3.00	1.69	1.47
3.25	1.82	1.54
3.50	1.99	1.63
3.75	2.24	1.72
4.00	2.70	1.87
4.25	3.80	2.04
4.35	4.37	2.13
4.45	4.82	2.21
4.50	4.96	2.30
4.55	5.06	2.42
4.65	5.54	2.59
4.75	6.02	2.75
4.85	6.81	3.10

Table 2 pH titration data of Glycine with Ni²⁺ at 35 ± 0.1°C in dioxan-water (50% v/v)

Ionic strength [I] = 0.10 mol dm⁻³ [HClO₄] = 0.010442 mol dm⁻³
[Gly] = 0.0083 mol dm⁻³ Initial volume = 30 ml

Volume of NaOH ml	pH meter reading	
	Gly	Ni ²⁺ -Gly
0.00	1.66	1.50
0.25	1.69	1.52
0.50	1.71	1.55
0.75	1.77	1.59
1.00	1.82	1.63
1.25	1.87	1.68
1.50	1.91	1.72
1.75	1.99	1.78
2.00	2.06	1.83
2.25	2.18	1.89
2.50	2.23	1.95
2.75	2.29	2.03
3.00	2.44	2.11
3.25	2.59	2.20
3.50	2.73	2.30
3.75	2.90	2.42

4.00	3.06	2.55
4.10	3.12	2.60
4.20	3.19	2.63
4.25	3.25	2.66

Table 3 pH titration data of Glycine and MDPT with Ni²⁺ at 35 ± 0.1°C in dioxan-water (50 % v/v)

Ionic strength [I] = 0.10 mol dm⁻³ [HClO₄]
 = 0.010442 mol dm⁻³
 [Gly] = 0.0083 mol dm⁻³ Initial volume = 30 ml

Volume of NaOH ml	pH meter Reading	
	Ni:[MDPT]:[Gly]	
0.00	1.56	
0.50	1.63	
1.00	1.70	
1.50	1.77	
2.00	1.84	
2.50	1.92	
3.00	2.06	
3.25	2.13	
3.50	2.20	
3.75	2.30	
4.00	2.39	
4.25	2.56	
4.50	2.71	
4.75	2.81	
4.80	2.91	
4.85	3.01	
4.90	3.22	
4.95	3.39	
5.00	3.54	
5.05	4.08	

Since more coordination sites are available for bonding the first ligand to a metal ion than for the second ligand, the $\Delta \log K$ should, in general, be negative with Ni²⁺ usually having a coordination number of four, the expected value for $\Delta \log K$ – 0.6, value markedly greater than this demonstrating a stabilisation of the ternary complex. In fact, positive values mean that it prefers to bond to the complex [MA] rather than to the solvated metal ion. $\log X$ is really a disproportionation constant. Statistically a value of $\log 4$ is to be expected, so that values for $\log X$ of greater than 0.6 suggest that stabilisation of the ternary complexes. The value of $\log X$ is clearly dependent on the stability of the binary bis complexes and since these bis complexes are not intermediate to the formation of the ternary complexes²⁶, the value of $\log X$ may not truly reflect the stability of the mixed complex. However, $\log X$ will tend to be less dependent than $\Delta \log K$ on differences in the charges on ligands A and B. Hence the choice between using $\Delta \log K$ and $\log X$ to give a measure of the stabilisation of ternary complexes depends on the particular comparison being made.

The association constant of glycine, assigned as ligands (B) and the stability constants of the parent binary complex of Ni(II) at 35°C in I = 0.1 mol dm⁻³ (NaClO₄) used for the computation of mixed ligand complex system is reported. The data of Ni-MDPT binary system estimated under identically experimental conditions are reported. $\log \beta$ values obtained for 1:1, 1:2 Ni(II)-MDPT complex compared favourably with values expected for glycine like mode of binding of MDPT. The Ni-A/glycine system showed the presence of one mixed complex of NiAB.

It appears that complex formation between MDPT and Ni(II). In the NiAB species involves the formation of chelate ring the comparison of $\log K_{NiAB}^{NiA}$ (Table 4) and $\log K_{NiB}^{Ni}$ clearly indicate that all the ligands form five membered chelate ring in the NiAB complex species.

Thus, NiAB species would contain five membered chelate ring since more coordination positions are available for binding the first ligand to metal ion than for second ligand, negative values for $\Delta \log K_{NiAB}$ are expected.

Table 4 Complex formation constants for the ternary complexes of MDPT-nickel with some normally bidentate L-amino acids at 35°C (NaClO₄) standard deviation are given in parentheses

Parameters	L-Gly
$\log \alpha_{HB}$	9.61
$\log \alpha_{H_2B}$	11.89
$\log \alpha_{H_3B}$	-
$\log K_{NiB}$	9.50 (2)
$\log K_{NiB_2}$	11.62
$\log K_{NiAB}$	19.00 (9)
$\log K_{NiAB}$	1.6
$\log X_{NiAB}$	7.6

Glycine ligand prefers to add Ni-MDPT binary complex rather than to aquated Ni(II). Also, the positive $\Delta \log K_{NiAB}$ values suggest that formation of ternary complex, Ni_{AB} is preferred over the binary complex of Ni_A or Ni_B.

However, the maximum amount of total Ni(II) present in the Ni_{AB} complex is only about maximum 40%, the lesser percentage of complex formation attributed to steric faster associated with five membered chelating ring in the species. Distribution of various species as a function of pH of various ternary system in Tables (5&6) and Figs. (2).

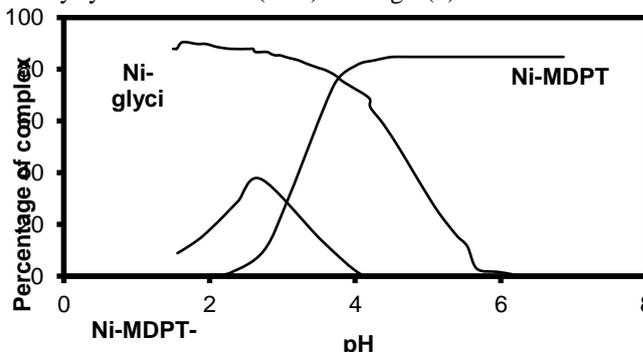


Fig. 2. Charge distribution curve for Ni-MDPT-Glycine system between pH Vs percentage of complex

Distribution diagram obtained in terms of percentage found Ni(II) as a function of pH in all four binary and ternary systems in the study, show the same quality features of formation of ternary complex species other binary complex species.

The existence of member of species in equilibrium of all pH values in ternary system where is certain pH regions. The concentration of one complex strongly predominant (Figs. 5&6).

Table 5Data for charge distribution of Ni- Glycine system pH versus percentage of complex

pH	Percentage of complex
1.50	87.9
1.53	87.9
1.55	87.9
1.63	90.5
1.83	89.8
1.95	89.8
2.11	88.6
2.30	87.9
2.55	87.9
2.60	87.9
2.63	86.7
2.79	86.7
2.84	86.0
2.90	85.4
2.97	85.4
3.04	84.8
3.12	84.2

Table 6Data for charge distribution of Ni-MDPT -Glycine system pH versus percentage of complex

pH	Percentage of complex
1.56	8.9
1.63	10.0
1.70	11.3
1.77	12.6
1.84	14.0
1.92	15.8
2.06	19.5
2.20	23.4
2.39	28.9
2.71	37.5
3.54	13.8
4.08	0.70
4.39	0.16
4.7	0.12
5.3	0.12

4. CONCLUSION

The present investigation describes the formation equilibria of binary and ternary complexes of nickel(II) involving adenine (A) and various biologically relevant ligands containing different functional groups. The ternary complexes of amino acids are formed in a stepwise process, whereby binding of nickel(II) to (A) is followed by ligation of the α -amino acids. The ternary complexes of sulphur ligands are formed by simultaneous reactions. The stability constants of complexes in solution have been calculated and their concentration distribution are evaluated.

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