

ORIGINAL ARTICLE

DETERMINATION OF THE STABILITY CONSTANTS OF MIXED LIGAND COMPLEX
OF NICKEL(II) WITH α -AMINO ACID

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ABSTRACT

Formation of binary and ternary complexes of Nickel(II) ions with biologically important α -amino acids, such as cysteine was investigated using the potentiometric technique at 35°C. The properties of mixed ligands were investigated and discussed. The acidity constants of the ligands and their stability constants were determined in 50% (v/v) Dioxane-water medium under experimental conditions. The ternary complex formation was found to occur in a stepwise manner. The stability of ternary complexes was investigated and compared with that of the corresponding binary complex in terms of the parameters, $D \log K$ and $\log X$. The concentration distribution of the species formed in the mixed ligand system was evaluated.

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

1.INTRODUCTION

Amino acids are of special importance among the other chemical substances since they form the basic constituents of living organisms. It is imperative to know the properties of amino acids in order to understand and explain their behavior and the synthesis of peptides, proteins and enzymes in living organisms. It is known that the reactions of peptides, proteins and enzymes with metal ions are of biochemical importance but they are yet to be thoroughly understood. The explanation of these phenomena in the biological systems can be possible only by the determination of protonation constants of the amino acids as well as their stability constants, which are a measure of their tendency to form complexes with other metal ions a medium similar to that of biological systems. It is observed that most of these determinations have been carried out in aqueous media¹⁻⁹. This may be attributed to the widespread belief that "in vivo" media are well represented by the aqueous media. In recent years, however, it has been reported that aqueous media are not suitable for biological in vivo reactions, on the contrary the biological media show lipophilic character and are better represented by non-aqueous media¹⁰. The number of studies in non-aqueous media is very limited in literature¹¹⁻¹³. It has been shown that plays an import role in biochemistry because it functions as anticonvulsant¹⁴ and also effective for the treatment of neuropathic pain in human and animal models¹⁵⁻¹⁷. We report

here to determine the stability constants of the complexes formed by cysteine with Nickel(II) in 50% (v/v) Dioxan-water medium at 35°C under nitrogen atmosphere using potentiometric method.

2. MATERIALS AND METHODS

Materials and solutions

All the chemicals used in this study were of AnalaR grade. Cyestine were under SD fine chemicals and used as such. Carbonate-free solution of NaOH (0.1 M) was prepared in double distilled water and estimated by standard method. 1.0 M KNO₃ and 5.0 · 10⁻³M Nickel(II) stock solutions were prepared from Analargrade samples and their purities were checked by potentiometric titration for acid and MDPT method for nickel(II)¹⁸.

Potentiometric procedure

pH metric titrations were carried out at 32°C (±0.1°C) in a double walled glass cell. The temperature control was achieved by means of water circulation from a thermostat. pH measurement was carried out on a SYSTRONIC digital pH/mV meter type 335 accurate to ±0.005 units and equipped with a glass electrode and saturated calomel electrode. The pH meter was calibrated before and after each titration set with suitable buffer solutions (pH 4.0 and 9.2).

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3. RESULTS AND DISCUSSION

Acidity constants of the free ligands

Representative potentiometric titration curves for the free and metal complexed ligands are depicted (cysteine) in Fig. 1. The acid dissociation constants of α -amino acids in 50% (v/v) Dioxan-water were determined from curves (a) and (d) using a computer program based on Irving-Rosotti pH titration techniques¹⁹. The values of the dissociation constants of cysteine were determined under the same experimental conditions (35°C, $I = 0.1$ M NaClO₄). The SCOGS²⁰ computer program was used to refine the overall protonation constants by minimizing the standard deviation of the fit (r fit) between the observed and calculated pH values.

The pK_a values obtained through the refinement of several sets of potentiometric data are given in Table 1. The pK_a values of amino acids show good agreement with the literature values after allowing for changes in experimental conditions and methods of calculation. It is worth mentioning that the pK₁^H values for α -amino acids changed little in anionic and neutral forms (A⁻, HA) but log K₂^H values changed appreciably with solvent composition. pK_a values increased with the increases in the amount of dioxan in the medium²¹.

Stability constants of the ternary complexes

The stability constants of both 1:1 and 1:2 binary complexes of the chosen ligands were determined at 35 ± 0.1 °C and $I = 0.1$ M NaClO₄. It can be observed that the stability constants of the different 1:2 metal–ligand complexes are lower than those of the corresponding 1:1 systems, as expected from statistical considerations. The Dlog K (log K₂-log K₁) values are negative. This is the normal trend in neutral ligands where the enthalpy is more favorable for a 1:1 species (exothermic) compared to a 1:2 species²².

The association constant of MDPT, L-cysteine, and 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)

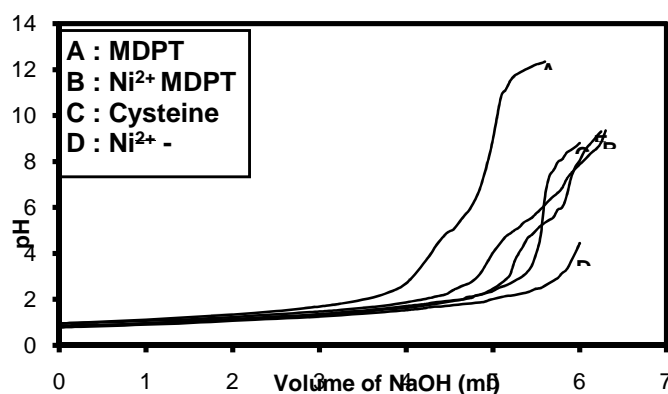


Fig. 1. pH metric titration curve for Ni²⁺ -MDPT - Cysteine system

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 Cys, 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

Volume of NaOH ml	pH meter reading	
	Cys	Ni ²⁺ -Cys
0.00	0.81	0.79
0.25	0.84	0.82
0.50	0.88	0.85
0.75	0.91	0.88
1.00	0.96	0.92
1.25	1.00	0.94
1.50	1.05	0.99
1.75	1.10	1.03
2.00	1.15	1.08
2.25	1.20	1.13
2.50	1.25	1.17
2.75	1.30	1.21
3.00	1.36	1.27
3.25	1.44	1.32
3.50	1.51	1.39
3.75	1.61	1.46
4.00	1.71	1.54
4.10	1.75	1.58

4.20	1.79	1.62
4.25	1.82	1.66

Table 3 pH titration data of Cys, 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
 [Cys] = 0.0037 mol dm⁻³ Initial volume = 30 ml
 [Ni²⁺] = 0.0015 mol dm⁻³ [MDPT]
 = 0.00517 mol dm⁻³

Volume of NaOH ml	pH meter Reading
	Ni:[MDPT]:[Cys]
0.00	0.87
0.50	0.90
1.00	0.97
1.50	1.05
2.00	1.12
2.50	1.22
3.00	1.32
3.25	1.40
3.50	1.46
3.75	1.56
4.00	1.64
4.25	1.76
4.50	1.91
4.75	2.07
4.80	2.17
4.85	2.21
4.90	2.27
4.95	2.36
5.00	2.46
5.05	2.58

The affinity that he has for bonding to the aquated metal ion and to the complex [MA]. Since more coordination side are available for bonding the first ligand to a metal ion than for the second ligand, the logK should, in general, negative with Ni²⁺ usually having a coordination number of four, the expected value for logK - 0.6, value markedly greater than this demonstrating a stabilisation of the ternary complex. In fact, positive values mean that prefers to bond to the complex [MA] rather than to the solvated metal ion. log X is really a dispropagation constant. Statistically a value of log4 is to be expected, so that values for logX 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 the formation of the ternary complexes²³, the value of logX may not truly reflect the stability of the mixed complex. However, logX will tend to be less dependent than logK on differences in the charges on ligands A and B. Hence the choice between using logK and logX to give a measure of the stabilisation of ternary complexes the depend on the particular comparison being made.

The association constant of L-cysteine, 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. logK values obtained for 1:1, 1:2 Ni(II)-MDPT complex compared favourably with values expected for glycine likes mode of binding of MDPT (Table 5). The Ni-A/cysteine 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.

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-Cys
logK _{HB}	10.12
logK _{H₂B}	18.43
logK _{H₃B}	19.90
logK _{NiB}	11.00 (2)
logK _{NiB₂}	22.00 (1)
logK _{NiAB}	23.50 (4)
logK _{NiAB}	4.6
logX _{NiAB}	9.2

L-cysteine ligand prefers to add Ni-MDPT binary complex rather than to aquatedNi(II). Also, the positive ΔlogK_{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. The stability constant data indicate that in addition of cysteine

is more favoured in ligand. Distribution of various species as a function of pH of various ternary system in Tables (5&6) and Figs. (2).

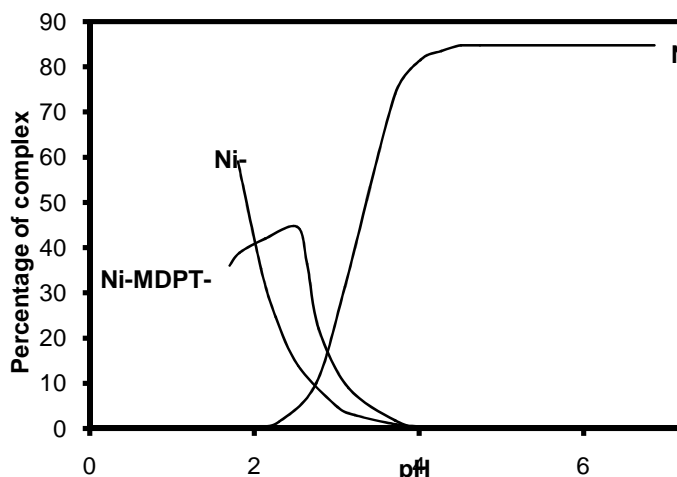


Fig. 2. Charge distribution curve for Ni-MDPT-Cysteine system between pH Vs percentage of complex

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 (Fig. 2).

Table 2 Data for charge distribution of Ni-cysteine system pH versus percentage of complex

PH	Percentage of complex
1.8	59.05
2.08	35.31
2.26	24.62
2.53	13.92
3.01	4.79
3.22	2.98
3.72	0.94
4.1	0.34
4.51	0.07

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

PH	Percentage of complex
1.7	36.02
1.82	38.91
2.13	42.01
2.52	44.61
2.64	36.41

2.78	22.08
3.14	9.05
3.71	1.75
4.08	0.065

4. CONCLUSION

The pH metric studies on Ni(II) (A)-cysteine (B) ternary complex systems at 32°C and I = 0.1 M (NaClO₄) show that the ternary complex species have, in general, higher stability compared to the binary analogs. The results indicate that the coordination mode of ligands A and B to be the same in the binary and ternary complex species. In aqueous Dioxan medium, the stability constants of the binary, and ternary systems possess higher values compared with the binary and ternary systems in the aqueous medium, which indicates that aqueous Dioxan medium is more favoured for complex formation than in aqueous medium.

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