

**FORMATION OF ZINC(II) WITH PHENANTHROLINE ACID MIXED LIGAND METAL COMPLEX IN AQUEOUS 1,4-DIOXAN MEDIUM**

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**ABSTRACT**

In this work, we present the study of the ternary zinc(II) complexes with phenanthroline acid. The relative stability of the ternary complexes compared to the binary ones were evaluated considering the values of  $\Delta \log K$ ,  $\log X$  and % R. S. Species distribution diagrams as a function of pH were briefly discussed. The stability of the mixed ligand metal complexes are determined by potentiometric titrations and the stability of the complexes are discussed in terms of basicity and steric factor for the Schiff's base derived from 3-ethyl-2,6-diphenylpiperidine-4-one with thiocarbohydrazides, which is most important application in the biological systems, catalytic activities and electrochemical properties. The synthesized EDPT ligand were characterized by Microanalyser and IR techniques. The ligand EDPT was determined by standard method of nitrogen and sulphur; Zn:19.40 (19.83), S: 9.00 (9.06), for EDPT.

**Key Words:** EDPT, IR, Microanalyser, adipicacid, Potentiometric technique .

**1.INTRODUCTION**

The lack of published experiments on determination of stepwise equilibrium constants is striking in view of the prominence given to coordination chemistry and complex ion equilibrium calculations<sup>1</sup>. Student experiments which consider only one predominant species (usually using Job's method) give no idea of the more common complexity met in most systems consisting of metal ions and the ligands NH<sub>3</sub>, halide ions, SCN<sup>-</sup>, etc. The detailed thought that is given to a laboratory experiment and its calculations should help clarify the subject, introduced this topic because of its complexity may be inspired to do so after considering the consistent and clarifying mathematical treatment of a variety of complex equilibria by Butler<sup>2</sup>.

In general, many experimental and mathematical difficulties are encountered in the determination of formation constants, as examination of the treatise by Rossotti and Rossotti<sup>3</sup> will verify. However, there are a few systems favorable for student investigation. Bjerrum's method for transition metal ion amines<sup>4</sup> can give extensive data in a short time and lead to a good approximation to the first four copper-amine formation constants. The graphical method can give the student a clear grasp of the functional relations involved.

The following adaptation was used with good results by advanced quantitative chemistry students and might serve in any course treating equilibria quantitatively. The experimental work was completed easily in one afternoon by students working in pairs. They had previously prepared standard solutions and were familiar with the pH meter. The ammine systems with Ni(II), Ag(I), Zn(II), Cd(II), and Co(II) might also be assigned to different students or groups. Air oxidation of Co(II) under the conditions required is said to be slow enough not to interfere<sup>4</sup>.

A survey of literature reveals that a number of thiocarbohydrazide and their derivatives have been used extensively to synthesise various derivatives of different heterocyclic compounds<sup>5-9</sup>. 3-Mercapto-1,5-diphenylformazan (dithizone, dzH) was first prepared by Emil Fischer and Bestorn<sup>10</sup> over a century ago. In 1925 Hellmut Fischer<sup>11</sup> introduced dithizone as a versatile analytical reagent and subsequently exploited its use for the solvent extraction and quantitative estimation of a number of metal ions of industrial and toxicological interest. The conditions for the isolation and determination of a wide variety of metals as their dithizonate or substituted dithizonate have been well reviewed<sup>12,13</sup>. The ligand forms neutral complexes with soft metal ions with several 'border line' metals.

Symmetric and asymmetric derivatives of carbohydrazone and thiocarbohydrazone have been studied due to their possibilities as analytical reagents. Thiocarbohydrazone are compounds with known carcinostatic and the antiviral activity of such ligands and their complexes were linked to these properties, which allow various practical applications<sup>14-21</sup>.

Thiocarbohydrazone and its hydrazones act as a neutral bidentate ligand due to the presence of the azomethine (-C=N-), hydrazine (-NH-NH<sub>2</sub>) and thione (>C=S) groups in the molecule. Protonation equilibrium constants of thiocarbohydrazone have been reported by Braibantiet al.<sup>22</sup>. The association constants of this ligand with divalent metals in acidic solutions have been determined. Burns<sup>23</sup> has studied complexes of this ligand with Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) in the solid state. Burns<sup>23</sup> concluded, on the basis of their infrared spectra, that they contain a ring of the thio-ketonic form. Campiet al<sup>24</sup> have studied the association equilibria of the analogous ligand carbohydrazone, O=C(NHNH<sub>2</sub>)<sub>2</sub>, with divalent metals. They suggested that this ligand chelates through N, N forming a six membered ring. The discovery that the molecule of thiocarbohydrazone is itself in *trans* configuration further supports this hypothesis. The formation of analogous ring in complexes of thiocarbohydrazone (S, N donor) and in complexes of carbohydrazone (O,N donor) is confirmed by the small but sufficient, difference between the stability constants for the two ligands. Infact, for nickel, K1 (caz) > K1 (tcaz) where as for the other metals the reverse is true. This is in accordance with the conclusions of Arhlandet al.<sup>25</sup>, Arhland<sup>26</sup> and Suzuiki and Yamasaki<sup>27</sup> who affirm that affinity of zinc uncharged is less sulfur than for oxygen while affinity of nickel is more for sulfur than for oxygen.

The study of the protonation equilibria<sup>22</sup> of thiocarbohydrazone has shown that in acidic media the thiocarbohydrazone can associate with two protons, one for the each hydrazide group, thus maintaining the thio-ketonic form. On the other hand in alkaline media the molecule probably changes into a thioenolic form because it is deprotonated twice. Braibantiet al.<sup>22</sup> have determined the association equilibria of this ligand with divalent metals in acidic media. In alkaline media precipitation of solid substances makes it possible to study the equilibria by potentiometric or spectrophotometric methods. Titrations with Cu(II) and Cd(II) failed because of precipitation of solid compounds even in acidic media; Mn does not show detectable association.

The equilibrium constants of thiocarbohydrazone (tcaz) with divalent metals are closely related to the equilibrium constant presented by carbohydrazone (caz)<sup>24</sup>. The equilibrium constants of these ligands (Table 1) show how they probably belong to a common family. For these ligands five membered ring chelates can be postulated.

## 2. MATERIAL AND METHODS

### Preparation of 3-ethyl-2,6-diphenyl piperidin-4-thiocarbohydrazone

An equimolar (0.05 mol dm<sup>-3</sup>) mixture of 3-ethyl-2,6-diphenylpiperidine-4-one<sup>28</sup> and thiocarbohydrazone<sup>23</sup> 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 bucker 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.

### Characterization of ligands

Microanalyser and IR techniques characterized the ligand EDPT. IR spectra were recorded on a JASCO 700 spectrophotometer in KBr pellets. Microanalysis of the ligand EDPT was determined by standard method nitrogen<sup>29</sup> and sulphur<sup>29</sup>; Zn:19.40 (19.83), S: 9.00 (9.06), for EDPT.

### Metal ion solutions

Approximately 0.01 mol dm<sup>-3</sup> stock solution of zinc ion, zinc(II) per chloride and the metal solutions were standardized using reported procedures<sup>29</sup>.

### 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 (Table 1).

Table 1 Calculated and observed values of pH

Conc. of [H <sup>+</sup> ]	Calculated pH	Observed pH
$3.4713 \times 10^{-4}$	3.45	3.51
$6.9482 \times 10^{-4}$	3.16	3.21
$1.0422 \times 10^{-3}$	2.98	3.02
$1.3896 \times 10^{-3}$	2.85	2.90
$1.7370 \times 10^{-3}$	2.76	2.80

$$\text{Intercept} = -0.028$$

$$r = 0.9998$$

The following mixture a, b, c, d were prepared from each system and titrate against standard alkali solution using Bjerrum-Calvin pH titration technique.

- 3 ml of perchloric acid (0.10422 mol dm<sup>-3</sup>) + 3 ml of sodium perchlorate (1 mol dm<sup>-3</sup>) + 15 ml dioxan + 9 ml of water.
- 3 ml of perchloric acid (0.10422 mol dm<sup>-3</sup>) + 3 ml of sodium perchlorate (1 mol dm<sup>-3</sup>) + 5 ml of primary ligands/secondary ligand (0.01 mol dm<sup>-3</sup>) + appropriate amount of dioxan and water.
- 3 ml of perchloric acid (0.10422 mol dm<sup>-3</sup>) + 3 ml of sodium perchlorate (1 mol dm<sup>-3</sup>) + 2 ml of primary ligand/3ml of secondary ligand (0.01 mol dm<sup>-3</sup>) + 3 ml of zinc ion (0.01 mol dm<sup>-3</sup>) + appropriate amount of 1,4-dioxan + appropriate amount of water.
- 3 ml of perchloric acid (0.1 mol dm<sup>-3</sup>) + 3 ml of sodium perchlorate (1 mol dm<sup>-3</sup>) + 2 ml of primary ligand (0.01622 mol dm<sup>-3</sup>) and 3ml of secondary ligand (1:1) + appropriate amount of 1,4-dioxan and appropriate amount of

water + 3 ml of zinc ion (0.01 mol dm<sup>-3</sup>).

$$\begin{aligned} \log K &= \log K_{MAB}^{MA} - \log K_{MB}^M \\ &= \log K_{MAB} - \log K_{MA}^M \end{aligned} \quad (5)$$

### 3.RESULT AND DISCUSSION

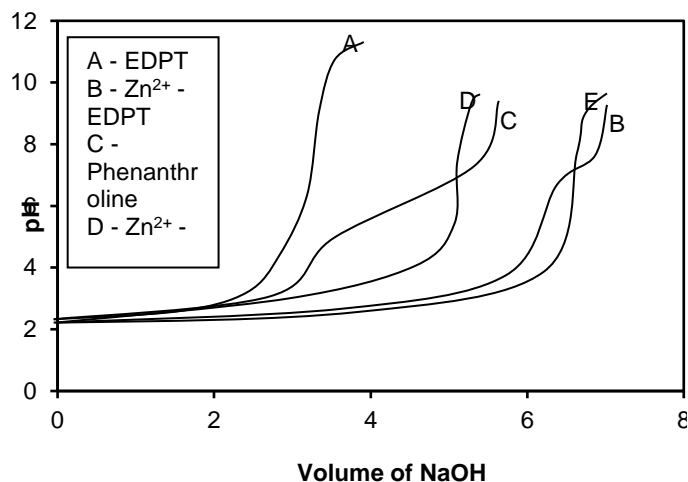
#### IR spectral studies

A comparison of IR spectra of the ligands with starting compounds is also done to confirm the condensation between the starting compounds. The ligands spectra show a broad band around 3410-3390 cm<sup>-1</sup><sup>23</sup> which is attributed to the presence of secondary amine of piperidine ring nitrogen and thiocarbohydrazideazine group (-NH - NH<sub>2</sub>). The band due to NH<sub>2</sub> wagging vibrations appear in the region 750-756 cm<sup>-1</sup><sup>30</sup>. The disappearance of the bands pertains to the ketocarbonyl at 1705-1700 cm<sup>-1</sup> of 3-ethyl-2,6-diphenylpiperidin-4-one, and new band appeared at 1625 cm<sup>-1</sup> of EDPT is attributed to the formation of azomethine (C=N) group<sup>31-34</sup>. The absence of any band in the region 2500-2600 cm<sup>-1</sup> confirms the presence of thioamide (N-C-N) group in the thione form exclusively<sup>23,29</sup>. The other stretching vibrational frequencies are unaltered.

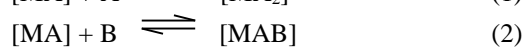
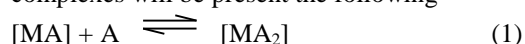
#### Ternary Zinc(II) – Phenanthroline acid complexes

The association constant of EDPT, phenanthroline acid, and stability constant of binary and ternary Zn determined in 50% (v/v) 1-4-dioxane water mixture at 35°C and data are given in Tables (2-6) and Fig. (1)

Fig. 1. pH metric titration curve for Zn<sup>2+</sup>-EDPT-Phenanthroline system



When a metal ion is equilibrium with two different ligands, A and B both of which can form *bis* complexes with the metal, equilibria (1)-(4) forming simple non-protonated *bis* complexes will be present the following



Sigel<sup>32</sup>, two equilibrium constants involved in ternary complexes can be defined, logK which

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

Ionic strength [I] = 0.1 mol dm<sup>-3</sup>[EDPT] = 0.00517 mol dm<sup>-3</sup>  
 [HClO<sub>4</sub>] = 0.010442 mol dm<sup>-3</sup>Initial volume = 30 ml  
 [NaOH] = 0.1271 mol dm<sup>-3</sup>V = volume of 0.1271 mol dm<sup>-3</sup>NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.20	3.10	5.87
0.50	2.30	3.12	6.01
1.00	2.42	3.14	6.11
1.50	2.56	3.16	6.35
1.75	2.67	3.18	6.51
2.00	2.79	3.20	6.91
2.05	2.82	3.22	7.27
2.13	2.88	3.24	7.71
2.15	2.90	3.23	8.11
2.20	2.93	3.28	8.55
2.25	2.97	3.30	8.83
2.30	2.99	3.32	9.29
2.35	3.04	3.34	9.58
2.40	3.15	3.36	9.82
2.45	3.25	3.38	9.99
2.52	3.35	3.40	10.03
2.55	3.37	3.42	10.12
2.60	3.46	3.44	10.35
2.65	3.55	3.46	10.40
2.70	3.85	3.48	10.50
2.75	4.00	3.50	10.59
2.80	4.30	3.52	10.66
2.85	4.90	3.56	10.84
2.90	5.01	3.61	10.99
2.95	5.17	3.64	11.03
2.95	5.17	3.68	11.10
3.00	5.33	3.72	11.16
3.02	5.50	3.76	11.25
3.04	5.60	3.80	11.32
3.06	5.70	3.84	11.36
3.08	5.80	3.88	11.38

**Table 3 pH titration data of Zn<sup>2+</sup>-EDPT at 35 ± 0.1°C in dioxan-water (50 % v/v)**Ionic strength [I] = 0.1 mol dm<sup>-3</sup>[HClO<sub>4</sub>] = 0.010442 mol dm<sup>-3</sup>[Zn<sup>2+</sup>] = 0.0015 mol dm<sup>-3</sup>[EDPT] = 0.00517 mol dm<sup>-3</sup>V = volume of 0.1271 mol dm<sup>-3</sup>NaOH. Initial volume = 30 ml

Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.27	4.75	3.00	6.24	6.45
0.20	2.30	4.80	3.02	6.26	6.56
0.40	2.33	4.85	3.04	6.28	6.65
0.60	2.34	4.90	3.06	6.30	6.75
0.80	2.35	4.95	3.10	6.32	6.79
1.00	2.37	5.00	3.13	6.34	6.85
1.20	2.38	5.05	3.15	6.36	6.93
1.40	2.40	5.10	3.16	6.38	6.97
1.60	2.42	5.15	3.19	6.40	7.01
1.80	2.43	5.20	3.22	6.42	7.04
2.00	2.45	5.25	3.25	6.44	7.08
2.20	2.46	5.30	3.29	6.46	7.12
2.40	2.48	5.35	3.33	6.48	7.15
2.60	2.50	5.40	3.38	6.50	7.19
2.80	2.52	5.45	3.40	6.52	7.22
3.00	2.56	5.50	3.46	6.54	7.26
3.20	2.58	5.55	3.52	6.56	7.29
3.40	2.62	5.60	3.58	6.58	7.33
3.60	2.70	5.65	3.65	6.60	7.36
3.80	2.74	5.70	3.77	6.62	7.39
4.00	2.76	5.75	3.91	6.64	7.41
4.05	2.77	5.80	4.05	6.66	7.45
4.10	2.79	5.85	4.24	6.68	7.49
4.15	2.80	5.90	4.45	6.70	7.54
4.20	2.81	5.95	4.78	6.72	7.56
4.25	2.82	6.00	5.02	6.74	7.61
4.30	2.83	6.02	5.14	6.76	7.66
4.35	2.84	6.04	5.26	6.78	7.73
4.40	2.86	6.08	5.40	6.80	7.80
4.40	2.87	6.10	5.53	6.82	7.93
4.45	2.89	6.12	5.65	6.84	8.06
4.50	2.91	6.14	5.77	6.86	8.48
4.55	2.93	6.16	5.89	6.88	8.89
4.60	2.94	6.18	6.01	6.90	9.21
4.65	2.96	6.20	6.17		
4.70	2.98	6.22	6.33		

**Table 4 pH titration data of Phenanthroline at 35 ± 0.1°C in dioxan-water (50 % v/v)**Ionic strength [I] = 0.1 mol dm<sup>-3</sup>[HClO<sub>4</sub>] = 0.010442 mol dm<sup>-3</sup>Phenanthroline = 0.0039661 mol dm<sup>-3</sup> Initial volume = 30 ml  
V = volume of 0.1271 mol dm<sup>-3</sup>NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.16	3.40	4.81	4.65	6.45
0.20	2.18	3.45	4.93	4.70	6.51
0.40	2.23	3.50	5.04	4.75	6.57
0.60	2.26	3.55	5.11	4.80	6.62
0.80	2.30	3.60	5.18	4.85	6.68
1.00	2.34	3.65	5.25	4.90	6.74
1.20	2.38	3.70	5.33	4.95	6.80
1.40	2.48	3.75	5.39	5.00	6.87
1.60	2.58	3.80	5.45	5.05	6.94
1.80	2.66	3.85	5.50	5.10	6.99
2.00	2.73	3.90	5.56	5.15	7.06
2.20	2.77	3.95	5.63	5.20	7.14
2.40	2.84	4.00	5.69	5.25	7.25
2.60	3.02	4.05	5.75	5.30	7.36
2.80	3.20	4.10	5.81	5.35	7.47
2.85	3.32	4.15	5.87	5.40	7.60
2.90	3.44	4.20	5.93	5.42	7.87
3.00	3.56	4.25	5.99	5.44	8.04
3.05	3.68	4.30	6.05	5.46	8.14
3.10	3.81	4.35	6.11	5.48	8.35
3.15	4.00	4.40	6.16	5.50	8.56
3.20	4.19	4.45	6.22	5.54	8.98
3.25	4.38	4.50	6.28	5.56	9.34
3.30	4.57	4.55	6.34		
3.35	4.69	4.60	6.39		

**Table 5** pH titration data of Phenanthroline with  $Zn^{2+}$  at  $35 \pm 0.1^\circ C$  in dioxan-water (50 % v/v)

Ionic strength  $[I] = 0.1 \text{ mol dm}^{-3}$   $[HClO_4] = 0.010442 \text{ mol dm}^{-3}$   
 Phenanthroline =  $0.0039661 \text{ mol dm}^{-3}$  Initial volume = 30 ml  
 $[Zn^{2+}] = 0.0015 \text{ mol dm}^{-3}$  V = volume of  $0.1271 \text{ mol dm}^{-3}$  NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.16	4.30	3.90
0.25	2.19	4.35	3.95
0.50	2.21	4.40	4.00
0.75	2.27	4.45	4.02
1.00	2.42	4.50	4.08
1.25	2.47	4.55	4.14
1.50	2.51	4.60	4.20
1.75	2.59	4.70	4.32
2.00	2.66	4.75	4.40
2.25	2.78	4.80	4.48
2.50	2.83	4.85	4.63
2.75	2.89	4.90	4.78
3.00	3.04	4.95	5.06
3.25	3.19	4.99	5.39
3.50	3.23	5.05	7.64
3.75	3.50	5.10	8.07
4.00	3.66	5.15	9.06
4.10	3.72	5.20	9.26
4.20	3.79	5.25	9.46
4.25	3.85	5.30	9.60

**Table 6** pH titration data of Phenanthroline and EDT with  $Zn^{2+}$  at  $35 \pm 0.1^\circ C$  in dioxan-water (50 % v/v)

Ionic strength  $[I] = 0.1 \text{ mol dm}^{-3}$   $[HClO_4] = 0.010442 \text{ mol dm}^{-3}$   
 Phenanthroline =  $0.0039661 \text{ mol dm}^{-3}$  Initial volume = 30 ml  
 $[Zn^{2+}] = 0.0015 \text{ mol dm}^{-3}$   
 $[EDPT] = 0.00517 \text{ mol dm}^{-3}$   
 V = volume of  $0.1271 \text{ mol dm}^{-3}$  NaOH.

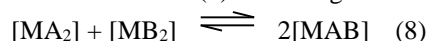
Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.20	5.70	3.37
0.50	2.11	5.75	3.40
1.00	2.16	5.80	3.44
1.50	2.21	5.85	3.50
2.00	2.28	5.90	3.54
2.50	2.35	5.95	3.60
3.00	2.44	6.00	3.66
3.50	2.53	6.05	3.80
4.00	2.64	6.10	3.91
4.50	2.77	6.15	4.00
5.00	2.96	6.20	4.08
5.05	2.98	6.25	4.15
5.10	3.01	6.30	4.24
5.15	3.03	6.35	4.30
5.20	3.06	6.40	4.74
5.25	3.09	6.45	5.50
5.30	3.11	6.50	7.21
5.35	3.15	6.55	8.42
5.40	3.17	6.60	8.80
5.45	3.20	6.65	8.98
5.50	3.24	6.70	9.19
5.55	3.28	6.75	9.34
5.60	3.30	6.80	9.50
5.65	3.34	6.85	9.64

refers to reaction (6)  $\log X$  [equation (7)] which

$$[MA] + [MB] \rightleftharpoons [MAB] + M \quad (6)$$

$$\log X = 2 \log \beta_{MAB} - \log \beta_{MA_2} - \log \beta_{MB_2} \quad (7)$$

refers to reaction (8). Thus  $\log K$  is a measure of the



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  $\Delta \log K$  should, in general, negative with  $Zn^{2+}$  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 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 the formation of the ternary complexes<sup>31</sup>, 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  $\log K$  on differences in the charges on ligands A and B. Hence the choice between using  $\log K$  and  $\log X$  to give a measure of the stabilisation of ternary complexes depend on the particular comparison being made.

The association constant of phenanthroline acid, assigned as ligands(B) and the stability constants of the parent binary complex of Zn(II) at 35°C in  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) used for the computation of mixed ligand complex system is reported. The data of Zn-EDPT binary system estimated under identically experimental conditions are reported. Log values obtained for 1:1, 1:2 Zn(II)-EDPT complex compared favourably with values expected for phenanthroline acid likes mode of binding of EDPT (Table 7). The Zn-A/ phenanthroline acid system showed the presence of one mixed complex of ZnAB.

It appears that complex formation between EDPT and Zn(II). In the ZnAB species involves the formation of chelate ring the comparison of  $\log K_{ZnAB}^{ZnA}$  (Table 7) and  $\log K_{ZnB}^{Zn}$  clearly indicate that all the ligands form five membered chelate ring in the ZnAB complex species.

Thus, ZnAB 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  $\Delta \log K_{ZnAB}$  are expected (eq. 9 and 10).

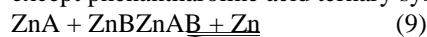
**Table 7 Negative logarithms of the acidity constants of the ligand (EDPT) and logarithms of the stability constants of the binary  $Zn^{2+}$  complexes ( $I = 0.1 \text{ mol dm}^{-3}$ ) at; 35°C**

System	Protonation / stability constants
A/EDPT	$pK_1 = 12.50$ $pK_2 = 16.62$
Zn-A/ Zn-EDPT	$\log \square_1 = 7.9$ $\log \square_2 = 7.9$

**Table 8 Complex formation constants for the ternary complexes of EDPT-Zinc with some normally bidentate L-amino acids at 35°C ( $\text{NaClO}_4$ ) standard deviation are given in parentheses**

Parameters	L-Phen
$\log \beta_{HB}$	9.24
$\log \beta_{H_2B}$	14.32 (2)
$\log \beta_{H_3B}$	-
$\text{Log} K_{ZnB}$	4.80
$\text{Log} K_{ZnB_2}$	-
$\text{Log} K_{ZnAB}$	18.90 (4)
$\Delta \log K_{ZnAB}$	1.5
$\Delta \log X_{ZnAB}$	7.8

But the  $\Delta \log K_{ZnAB}$  for the present investigation is positive except phenanthroline acid ternary system.



$$\Delta \log K_{ZnAB} = \log \beta_{ZnAB} - (\log \beta_{ZnA} + \log \beta_{ZnB}) \quad (10)$$

This indicates that Adipic acid ligand prefers to add Zn-EDPT binary complex rather than to aquated Zn(II). Also, the positive  $\Delta \log K_{ZnAB}$  values suggest that formation of ternary complex,  $Zn_{AB}$  is preferred over the binary complex of  $Zn_A$  or  $Zn_B$ .

However, the maximum amount of total Zn(II) present in the  $Zn_{AB}$  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 (8-11) and Figs. (2).

Distribution diagram obtained in terms of percentage found Zn(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. 2).

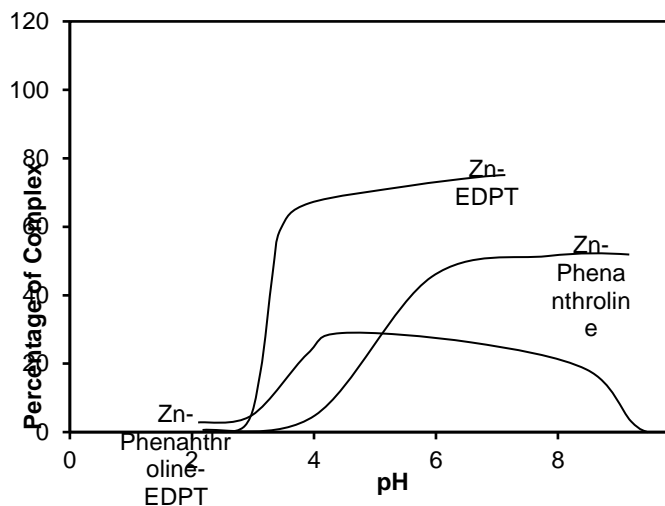


Fig. 2. Charge distribution for Zn-EDPT-Phenanthroline system between pH Vs Percentage of complex

Table 9 Data for charge distribution of Zn-EDPT system pH versus percentage of complex

pH	Percentage of complex
2.27	0.0067
2.37	0.0260
2.45	0.0362
2.48	0.0742
2.56	0.2298
2.79	0.46
2.89	1.49
3.10	9.28
3.30	29.2
3.58	62.0
4.78	70.6
5.53	72.2
6.33	73.2
6.65	74.6
6.79	74.7
7.08	74.7

Table 10 Data for charge distribution of Zn-Phenanthroline system pH versus percentage of complex

pH	Percentage of complex
2.16	0.120
2.27	0.176
2.42	0.210
2.66	0.320
2.83	0.413
3.04	0.472
3.23	0.622
3.85	0.846
4.14	1.621
4.4	2.600
4.63	3.780
4.63	4.61
4.54	11.5
4.85	17.8
5.6	25.4
6.11	30.7
7.71	47.5
9.36	51.4

**Table 11 Data for charge distribution of Zn-EDPT-Phenanthroline system  
pH versus percentage of complex**

pH	Percentage of complex
2.20	2.26
2.35	2.72
2.64	3.80
2.96	4.79
3.11	6.21
3.28	8.86
3.40	13.21
3.60	16.88
4.00	24.92
4.25	28.92
5.50	27.96
7.21	24.24
8.42	17.26
8.80	9.46
8.98	4.02
9.19	0.82
9.34	0.142
9.50	0.00121

### 3. CONCLUSION

The primary ligand 3-ethyl-2,6-diphenylpiperidin-4-onethiocarbohydrazone[EDPT] was prepared by condensation of 3-ethyl-2,6-diphenylpiperidin-4-one and thiocarbohydrazone in rectified spirit. The ligand was checked by TLC and melting point. The amino acids such as phenanthroline acid were used as secondary ligand in potentiometric titration technique in aqueous 1,4-dioxan (0.1 mol dm<sup>-3</sup>). The protonation constants are determined by SCOGS method. Computer programme is obtained; data are very close to reported value. The overall stability constant reveals that ternary complex formation is more favoured than binary complexes. The stability constant of phenanthroline acid is greater in this systems.

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