STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES OF NICOTINIC ACID WITH Zn(II) BY POTENTIOMETRIC TITRATION METHOD

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ABSTRACT

In this study, the overall stability constants of zinc (II) complex with nicotinic acid were determined by potentiometric titration in water,dioxane system. The titration were performed at 35°C, under Nitrogen atmosphere, and the ioni strength of the medium was maintained at 0.10 M by using sodium perchlorite. The formation curves of the complexes (n-p[L])were obtained by means of the titration data. Then the stability constants were determined in relation to these curves. The important result obtained was that the tendency of amino acids to form complex with zinc (II) was grater in Dioxan-water compared to water.

Keywords: Nicotinic acid,Dioxan-water, Stability constant, Potentiometric technique .

1.INTRODUCTION

Co-ordination compounds have always been a challenge to the inorganic chemists. In early days these compounds seemed to be unusual (hence the name "complex" ions) which defy the rules of valence. The modern study of co-ordination compounds begins with Alfred Werner and SophusMads Jorgensen.

Co-ordination chemistry pertains to the complexity of the compounds, which do not exist as individual, but as related groups often surrounding a metal ion in the center. For instance, in the conversion of carbon dioxide and water into carbohydrate in the plants, a co-ordination compound called chlorophyll [Mg^{2+} Complex][1,2] plays an important role. A similar iron complex known as hemoglobin[3,4] operates in the red blood cells as carrier of oxygen. Co-ordination compounds are conveniently formulated as consisting of a central atom or ion, surrounded by a set [usually 2 to 9] of other atoms, ion or groups, latter being called ligands *e.g.* NH_3. Ligands are classified on the basis of number of donor groups attached to the ligands, like monodentate (NH_3), bidentate (en), tridentate (terpyridine) and tetradentate (triethylenetetramine) etc.
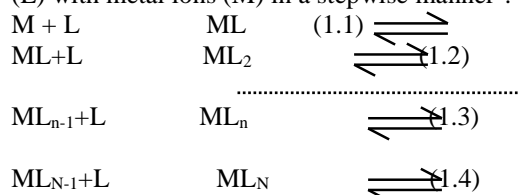
In solution, complex results from the reversible association of one or more metal ions and ligands. The chelate complex in which a metal is joined to two or more donor groups of a single molecule or ion are particularly important since they have exceptionally high stability and in many cases they

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possess remarkable properties. Although the number of known chelating and complexing agents is very large, the donor atoms, which undergo combination with metals, are restricted to the strongly non-metallic elements of V and VI. Two kinds of stabilities are recognized for the complexes.

    1. Thermodynamic stability
    2. Kinetic stability

Thermodynamic stability is the measure of the extent to which the complex will be formed when the system is in equilibrium. Kinetic stability refers to the speed with which transformations leading to the attainment of equilibrium will occur etal-ligand complex formation in solution (binary and ternary system): Stability of metal-ligand complexes and determination of stability constants

Formation and stability constants of metal-ligand complexes: Complexes results from reversible association of the ligands (L) with metal ions (M) in a stepwise manner[4]:

$$M + L \rightleftharpoons ML \quad (1.1)$$
$$ML + L \rightleftharpoons ML_2 \quad (1.2)$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$ML_{n-1} + L \rightleftharpoons ML_n \quad (1.3)$$
$$ML_{N-1} + L \rightleftharpoons ML_N \quad (1.4)$$

where, N is the maximum number of ligands (L) that can be associated with metal ion (M). The labile systems metal-ligand bonds make and break relatively quickly and the complexationequilibria (1.1 – 1.4) are established quite rapidly. The extent to which a particular complex is formed at equilibrium under a given set of conditions is given by its thermodynamics stability constant[5] (or the thermodynamics formation constant), which is the equilibrium constant of the

complexation reaction. In inert system metal-ligand equilibria are attained relatively due to slow making and breaking of metal-ligand bonds. The kinetic stability of a complex is due to its failure to attain the equilibrium with its constituents and is a measure of its slowness to attain the equilibrium.

The metal ion, the ligands and the complexes are solvated to different extents in solution. However, the solution of the metal ion is of considerable importance, in fact, complex formation in solution involves stepwise displacement of solvent molecules from the inner coordination sphere of the metal ion by the ligand groups:

M (solvent)$_n$ + L   M(solvent)$_{n-1}$ ⇌ solvent   (1.5)
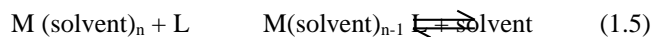
In majority of cases the values on n is 6 (octahedral complex) and often 4 (square planar or tetrahedral complex). In sufficiently dilute solutions the activity of the solvent remains practically unchanged during complexation and therefore the solvent molecules are often emitted from the chemical equation representing complexationequilibria. The activity (a_{ML_n}) of the complex ML$_n$ can be related to those of the metal ion, (a_M) and of the ligand (a_L), by the Law of Mass Action:

$$\beta_n^{\;0} = a_{ML_n} / a_M . a_L^{\;n} \qquad (1.6)$$

$$a_{ML_n} = \beta_n^{\;0} . a_M . a_L^{\;n} \qquad (1.7)$$

where the activity quotient β_n^0 is called the overall thermodynamic stability constant of the complex ML$_n$. The activity quotients for the individual step reactions [(1.1) – (1.4)] are given by (1.8):

$$K_{ML_n}^{ML_{n-1}} = a_{ML_n} / (a_{ML_{n-1}} . a_L) \quad (1.8)$$

and are called stepwise thermodynamic stability constants. The overall stability constant β_n^0 is the product of the successive step stability constants

$$\beta_n^0 = \frac{a_{ML_n}}{a_M a_L^n} = \frac{a_{ML}}{a_M a_L} \times \frac{a_{ML_2}}{a_{ML} a_L} \cdots \frac{a_{ML_{n-1}}}{a_{ML_{n-2}} a_L} \times \frac{a_{ML_n}}{a_{ML_{n-1}} a_L}$$

$$= (K_{ML}^M)^0 \, x (K_{ML_2}^{ML})^0 \, x ... x (K_{ML_{n-1}}^{ML_{n-2}})^0 \, x (K_{ML_n}^{ML_{n-1}})^0$$

or $\beta_n^0 = \pi_{n=1}^n (K_{ML_n}^{ML_{n-1}})^0$ (1.9)

In practice, concentration rather than activities of the species involved in the complexationequilibria are experimentally determinable. The concentration quotients, called the stoichiometric stability constants are related to the equilibrium concentrations of the metal ion, the ligand and the complex species involved in the complexationequilibria in an analogous manner as the thermodynamic stability constants are related to activities[6]. Thus the overall and stepwise stoichiometric stability constants β$_n$ and $K_{ML_n}^{ML_{n-1}}$ respectively of the complex ML$_n$ are given by

$$\beta_n = [ML_n]/([M][L]^n) = \beta_n^0 / \square\square_i^{\;vi} \qquad (1.10)$$

$$K_{ML_n}^{ML_{n-1}} = [ML_n]/([ML_{n-1}][L] = (K_{ML_n}^{ML_{n-1}})^0 / \pi \gamma_i^{\;v_i}$$
(1.11)

where, the terms in the square brackets represent concentrations of the respective species $\square_i$ are the stoichiometric numbers of participant species and $\square_i$ are the activity coefficients on the appropriate concentration scale.

Stoichiometric constants are thermodynamic constants, which are valid only at the standard state defined by the detailed composition of the solution and at a particular temperature of the experiment. Stoichiometric constants β$_n$ and $K_{ML_n}^{ML_{n-1}}$ determined in a certain experimental condition may be used to evaluate the thermodynamic constants β_n^0 and $(K_{ML_n}^{ML_{n-1}})^0$ with the help of equation (1.10) and (1.11) provided the activity coefficients (γ$_i$) under the experimental condition are available[7]. Unfortunately experimental value appropriate activity coefficients are seldom available for direct substitution in this equation. Usually stoichiometric constants are determined in medium of different ionic strengths and the values are extrapolated to zero ionic strength using Debye-Huckel extended equation[8], which related activity coefficients with the ionic strength. In most experimental work ionic strength and hence activity coefficients are kept practically constant by using excess of an inert salt such as NaClO$_4$, NaNO$_3$, KNO$_3$ etc. as supporting electrolyte, so that change in the concentration of the reactants and reduction and/or neutralization of change during complex formation do not alter the formal ionic strength of the solution, thereby, makes the stoichiometric stability constants meaningful, reliable and useful.

Formation or extents of formation of H$_3$O$^+$ ion is not assured in solvents either than water. H$_3$O$^+$ ions may be replaced by other species with references to the new solvent system. Measurement of hydrogen ion activity by means of a pH meter calibrated with aqueous buffer solutions is restricted to dilute aqueous solution only. Any variation in the ionic strength or composition of the solvent will cause large shift in the junction potential. For pH measurements in a mixed solvent, the appropriate temperature may be used for assuming complete ionization of strong acids in this solvent system. Hydrogen ion concentration [H$_3$O$^+$] or (simple [H$^+$] for such a system can be related to the pH meter reading (pH) by the following relation[9-12].

(pH) = -log [H] – log U = p[H] – log U (1.12)

where U is a function of ionic strength and composition of the solvent medium but it is independent of [H$^+$]. Thus hydrogen ion concentration [H$^+$] in any aqueous-organic solvent system can be obtained from the pH meter reading by graphical extrapolation of the relation (1.12) using a calibration curve constructed by plotting pH meter reading against –log[H$^+$] of a series of solution of known hydrogen ion concentration in the experimental solvent system at the desired temperature.

2.MATERIAL AND METHODS

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

An equimolar (0.05moldm^{-3}) mixture of 3-ethyl-2,6-diphenylpipiridine-4-one[28] and thiocarbohydrazide[13] 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 stream bath and poured into de-ionized water. The pale yellow colored product formed was filtered in a bucker funnel, dried and was

recrystalled 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[14] and sulphur[15]; Zn:19.40 (19.83), S: 9.00 (9.06), for EDPT.

Metal ion solutions

Approximately 0.01 mol dm^{-3} stock solution of zinc ion, zinc(II) per chloride and the metal solutions were standardized using reported procedures[16].

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$^+$]	Calculated pH	Observed pH
3.4713×10^{-4}	3.45	3.51
6.9482×10^{-4}	3.16	3.21
1.0422×10^{-3}	2.98	3.02
1.3896×10^{-3}	2.85	2.90
1.7370×10^{-3}	2.76	2.80

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.

a) 3 ml of perchloric acid (0.10422 mol dm^{-3}) + 3 ml of sodium perchlorate (1 mol dm^{-3}) + 15 ml dioxan + 9 ml of water.

b) 3 ml of perchloric acid (0.10422 mol dm^{-3}) + 3 ml of sodium perchlorate (1 mol dm^{-3}) + 5 ml of primary ligands/secondary ligand (0.01 mol dm^{-3}) + appropriate amount of dioxan and water.

c) 3 ml of perchloric acid (0.10422 mol dm^{-3}) + 3 ml of sodium perchlorate (1 mol dm^{-3})+2 ml of primary ligand/3ml of secondary ligand (0.01 mol dm^{-3}) + 3 ml of zinc ion (0.01 mol dm^{-3}) + appropriate amount of 1,4-dioxan + appropriate amount of water.

d) 3 ml of perchloric acid (0.1 mol dm^{-3}) + 3 ml of sodium perchlorate (1 mol dm^{-3}) + 2 ml of primary ligand (0.01622 mol dm^{-3}) 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^{-3}).

3. RESULT AND DISCUSSION

The acid dissociation constants of the ligands and the formation constants of their binary complexes were previously reported[17].

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^{-1}[18] which is attributed to the presence of secondary amine of piperidine ring nitrogen and thiocarbohydrazideazine group

(-NH - NH$_2$). The band due to NH$_2$ wagging vibrations appear in the region 750-756 cm^{-1}[19.] The disappearance of the bands pertains to the ketocarbonyl at 1705-1700 cm^{-1} of 3-ethyl-2,6-diphenylpiperidin-4-one, and new band appeared at 1625 cm^{-1} of EDPT is attributed to the formation of azomethine (C=N) group[20-24]. The absence of any band in the region 2500-2600 cm^{-1} confirms the presence of thioamide (N-C-N) group in the thione form exclusively[25-29]. The other stretching vibrational frequencies are unaltered.

Ternary Zinc(II) – Nicotini acid complexes

The association constant of EDPT, Nicotinic 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 (2-5) and Fig. (1)
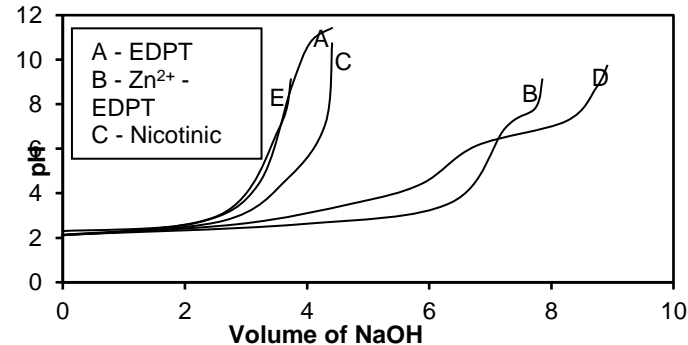

Fig. 1. pH metric titration curve for Zn^{2+}-EDPT-Nicotinic acid system

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

$$[MA] + A \rightleftharpoons [MA_2] \qquad (1)$$
$$[MA] + B \rightleftharpoons [MAB] \qquad (2)$$
$$[MB] + A \rightleftharpoons [MAB] \qquad (3)$$
$$[MB] + B \rightleftharpoons [MB_2] \qquad (4)$$
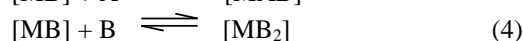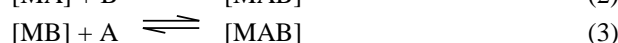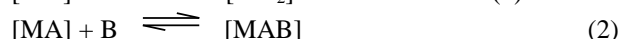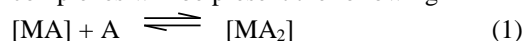
Sigel[30], two equilibrium constants involved in ternary complexes can be defined, logK which

$$\Box \log K = \log K_{MAB}^{MA} - \log K_{MB}^{M}$$
$$= \log K_{MAB} - \log K_{MA}^{M} \qquad (5)$$

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

Ionic strength [I] = 0.1 mol dm^{-3} [EDPT] = 0.00517 mol dm^{-3}

[HClO$_4$] = 0.010442 mol dm^{-3} Initial volume = 30 ml

[NaOH] = 0.1271 mol dm^{-3} V = volume of 0.1271 mol dm^{-3} NaOH.

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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^{2+}-EDPT at 35 ± 0.1ºC in dioxan-water (50 % v/v)

Ionic strength [I] = 0.1 mol dm^{-3} [HClO$_4$] = 0.010442 mol dm^{-3}

[Zn^{2+}] = 0.0015 mol dm^{-3} [EDPT] = 0.00517 mol dm^{-3}

V = volume of 0.1271 mol dm^{-3}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 Nicotinic acid at 35 ± 0.1ºC in dioxan-water (50 % v/v)

Ionic strength [I] = 0.1 mol dm^{-3}

[HClO$_4$] = 0.010442 mol dm^{-3}

Nicotinic acid = 0.0020000 mol dm^{-3}

Initial volume = 30 ml

V = volume of 0.1271 mol dm^{-3}NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.14	3.55	5.65
0.20	2.17	3.60	5.81
0.40	2.21	3.65	6.00
0.60	2.25	3.70	6.30
0.80	2.30	3.75	6.60
1.00	2.35	3.80	6.99
1.20	2.40	3.82	7.50
1.40	2.45	3.84	8.00
1.60	2.51	3.86	8.79
1.80	2.58	3.88	9.50
2.00	2.66	3.90	10.73
2.20	2.76		
2.40	2.86		
2.60	3.03		
2.80	3.19		
3.00	3.28		
3.20	4.37		

3.25	4.58
3.30	4.79
3.35	5.00
3.40	5.20
3.45	5.35
3.50	5.55

Volume of NaOH ml	pH	Volume of NaOH ml	pH
5.60	5.66	6.80	6.87
5.65	5.71	6.85	6.91
5.70	5.76	6.90	6.95
5.72	5.81	6.95	7.00
5.74	5.86	7.00	7.04
5.76	5.91	7.05	7.09
5.78	5.96	7.10	7.14
5.80	6.01	7.15	7.19
5.90	6.11	7.20	7.24
6.00	6.21	7.25	7.31
6.05	6.25	7.30	7.38
6.10	6.30	7.35	7.45
6.15	6.35	7.40	7.52
6.20	6.39	7.45	7.67
6.25	6.43	7.50	7.82
6.30	6.47	7.55	7.97
6.35	6.52	7.60	8.11
6.40	6.56	7.65	8.12
6.45	6.60	7.70	8.93
6.50	6.64	7.72	9.29
6.55	6.68	7.84	9.79
6.60	6.72		
6.65	6.75		
6.70	6.79		
6.75	6.83		

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

Ionic strength $[I] = 0.1$ mol dm^{-3}

$[HClO_4] = 0.010442$ mol dm^{-3}

Nicotinic acid $= 0.0020000$ mol dm^{-3}

Initial volume $= 30$ ml

$[Zn^{2+}] = 0.0015$ mol dm^{-3} V = volume of 0.1271 mol dm^{-3}NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.05	4.45	3.72
0.20	2.08	4.50	3.76
0.40	2.11	4.55	3.80
0.60	2.14	4.60	3.83
0.80	2.18	4.65	3.87
1.00	2.22	4.71	3.91
1.20	2.26	4.75	3.95
1.40	2.30	4.80	3.99
1.60	2.34	4.85	4.03
1.80	2.39	4.90	4.08
2.00	2.45	4.95	4.13
2.20	2.52	5.00	4.18
2.40	2.58	5.05	4.25
2.60	2.66	5.10	4.33
2.80	2.75	5.15	4.41
3.00	2.84	5.20	4.49
3.20	2.94	5.25	4.59
3.40	3.05	5.30	4.70
3.60	3.18	5.35	4.85
3.80	3.30	5.40	5.00
4.00	3.42	5.42	5.08
4.05	3.45	5.44	5.16
4.10	3.48	5.46	5.24
4.15	3.51	5.48	5.32
4.20	3.53	5.50	5.40
4.25	3.56	5.52	5.47
4.30	3.59	5.54	5.51
4.35	3.64	5.56	5.56
4.40	3.68	5.58	5.61

Table 6 pH titration data of Nicotinic acid and EDPT with Zn^{2+}at $35 \pm 0.1°C$ in dioxan-water (50% v/v)

Ionic strength $[I] = 0.1$ mol dm^{-3} $HClO_4] = 0.010442$ mol dm^{-3}

Nicotinic acid $= 0.0020000$ mol dm^{-3} Initial volume $= 30$ ml

$[Zn^{2+}] = 0.0015$ mol dm^{-3}[EDPT] $= 0.00517$ mol dm^{-3}

V = volume of 0.1271 mol dm^{-3}NaOH.

Volume of NaOH ml	pH	Volume of NaOH ml	pH
0.00	2.05	2.86	4.86
0.20	2.10	2.88	4.94
0.40	2.17	2.90	5.05
0.60	2.20	2.92	5.13
0.80	2.23	2.94	5.21
1.00	2.27	2.96	5.28
1.20	2.32	2.98	5.35
1.40	2.38	3.00	5.39
1.60	2.45	3.02	5.45
1.80	2.54	3.04	5.51
2.00	2.62	3.06	5.61
2.20	2.82	3.08	5.71

2.40	3.03	3.10	5.94
2.45	3.13	3.12	6.11
2.50	3.28	3.14	6.39
2.55	3.40	3.15	6.69
2.60	3.55	3.18	7.00
2.65	3.84	3.20	7.49
2.70	4.14	3.22	8.00
2.75	4.78	3.24	8.87
2.80	4.62	3.26	9.04
2.82	4.70		
2.84	4.78		

refers to reaction (6) logX [equation (7)] which

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

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

refers to reaction (8). Thus logK is a measure of the

$$[MA_2] + [MB_2] \rightleftharpoons 2[MAB] \quad (8)$$

The affinity that be 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 ΔlogK should, in general, negative with Zn^{2+} usually having a coordination number of four, the expected value for ΔlogK – 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 dispropanation 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 complexes[31], 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 depend on the particular comparison being made.

The association constant of Nicotinic acid, assigned as ligands(B) and the stability constants of the parent binary complex of Zn(II) at 35°C in I = 0.1 mol dm^{-3} (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 nicotinic acid likes mode of binding of EDPT (Table 6). The Zn-A/ nicotinic 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$\Delta logK_{ZnAB}$are expected (eq. 9 and 10).
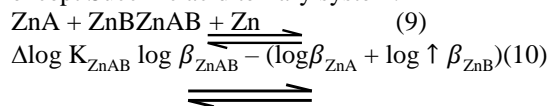
Table 7 Negative logarithms of the acidity constants of the ligand (EDPT) and logarithms of the stability constants of the binary Zn^{2+} complexes (I = 0.1 mol dm^{-3}) at; 35°C

System	**Protonation / stability constants**
A/EDPT	pK$_1$ = 12.50 pK$_2$ = 16.62
Zn-A/ Zn-EDPT	log β_1 = 7.9 log β_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 (NaClO₄) standard deviation are given in parentheses

Parameters	**L-Nic**
log☐$_{H_2B}$	17.28
log☐$_{H_3B}$	16.26
LogK$_{ZnB}$	12.28 (2)
LogK$_{ZnB_2}$	21.00 (1)
LogK$_{ZnAB}$	22.71 (4)
☐logK$_{ZnAB}$	3.2
☐logX$_{ZnAB}$	10.2

But the $\Delta logK_{ZnAB}$ for the present investigation is positive except Succinic acid ternary system.

$$ZnA + ZnB \rightleftharpoons ZnAB + Zn \quad (9)$$
$$\Delta log\, K_{ZnAB} \, log\, \beta_{ZnAB} - (log\beta_{ZnA} + log\uparrow\beta_{ZnB}) (10)$$

This indicates that nicotinic acid ligand prefers to add Zn-EDPT binary complex rather than to aquatedZn(II). Also, the positive $\Delta logK_{ZnAB}$ 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 interms 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-Nicotinic acid system between pH Vs Percentage of complex
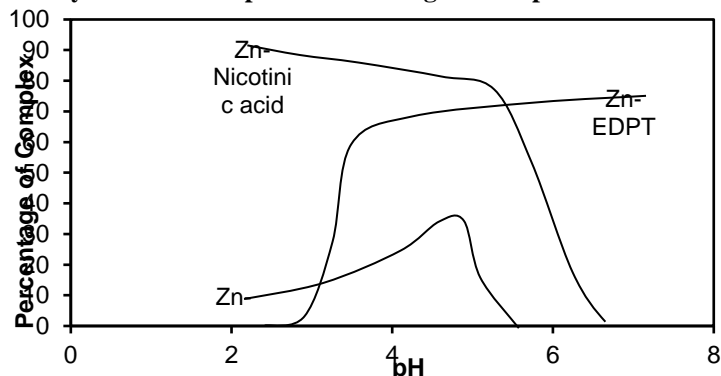
Table 9Data for charge distribution of Zn-EDPT system pH *versus* percentage of complex

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 10Data for charge distribution of Zn-Nicotinic acid system pH *versus* percentage of complex

pH	Percentage of complex
2.30	10.7
2.42	11.5
2.54	13.8
2.68	14.0
2.80	21.0
2.94	29.0
3.13	41.2
3.31	55.0
3.46	79.4
3.56	100
3.67	100
3.82	100
4.17	100
4.25	100
4.33	100
4.44	100

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

pH	Percentage of complex
2.28	10.3
2.36	15.4
2.45	22.2
2.57	25.6
2.68	27.6
2.80	28.2
2.90	29.6
3.10	25.4
3.24	23.2
3.44	22.6
3.56	21.4
3.68	20.2
3.85	19.5
4.10	17.51
4.22	13.62
4.32	8.46
4.50	6.42
4.80	4.16
4.98	2.61

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 thiocarbohydrazide in rectified spirit. The ligand was checked by TLC and melting point.The amino acids such as Nicotinic acid were used as secondary ligand in potentiometric titration technique in aqueous 1,4-dioxan (0.1 mol dm^{-3}). 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 Nicotinic acid is grater in this systems.

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