Unsymmetrical Schiff Base Complexes with transition metal: Stability constant study and effect of seed germination

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ABSTRACT: *N''*-[1-(5-chloro-2-hydroxyphenyl)ethylidene]-*N'''*-[1-(2-hydroxy-5-methylphenyl) ethylidene] carbonohydrazide (H_2L^1) and *N''*-[1-(2-hydroxy-5-methyl-3-nitrophenyl) ethylidene]-*N'''*-[1-(2-hydroxy-5-methyl phenyl) ethylidene] carbonohydrazide (H_2L^2**)** with Cu(II), Ni(II),Co(II)and Fe(III) spectrophotometrically investigated it shows 1:1 and 1:2 complex formation between the pH range of 3.0 to 6.0 and also studied by Jobs variation method at 0.1M ionic strength at $30^0C\pm1^0C$ specrtophotometrically. The conditional stability constants are determined for 1:1 complexes. Effect of H_2L^1 and H_2L^2 ligand and its complexes on seed germination is also studied.

***Keyword**:* **Unsymmetrical Schiff base, complexes, pH-metry study, spectrophotometric study, seed germination study.**

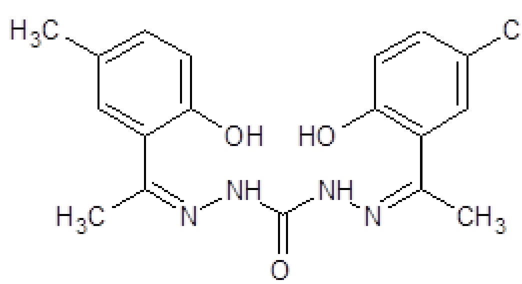
1. INTRODUCTION

Most of the symmetrical tetradentate Schiff base as ligands and their metal complexes have been widely studied due to their relevance in biological systems [1, 2] and some of them may be used as analytical reagent and catalysts in various chemical reactions [3]. Schiff bases offer a versatile and flexible series of ligands capable of binding with various metal ions to give complexes with suitable properties for many applications [4]. Schiff base ligands with N and O atoms are important and their metal complexes find wide spread applications as heterogeneous and homogeneous catalysts for the epoxidation of styrene [5]. The tetradentate ligands of the Schiff bases are of special interest owing to the great variety of analytical studies, stereochemical, catalytic and thermal studies of their complexes [6-9].

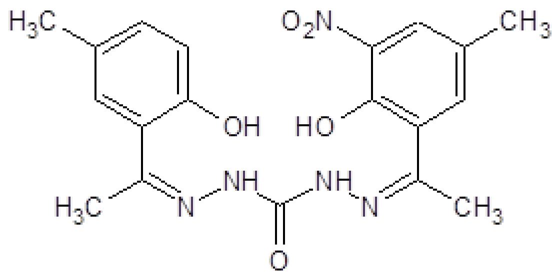
Much work on physical studies of metal complexes of symmetrical Schiff bases with different functional groups has been reported. However, as compared to symmetrical little research has been devoted to metal complexes of unsymmetrical ligands. Keeping in view analytical application of unsymmetrical Schiff bases are selected as a ligand in present study. Determination of formation constant and stability constant of metal complexes with various ligands have been an important parameter for predicting the mode of drug action of these drugs, hence it was thought of interesting to synthesize, characterize and physical studies of *N''*-[1-(5-chloro-2-hydroxyphenyl)ethylidene]-*N'''*- [1-(2-hydroxy-5-methylphenyl) ethylidene] carbonohydrazide (H_2L^1) and *N''*-[1-(2-hydroxy-5-methyl-3-nitrophenyl) ethylidene]-*N'''*-[1-(2-hydroxy-5-methyl phenyl) ethylidene] carbonohydrazide (H_2L^2**)** with some metal ion in the present study. Many researchers made significant contribution to these kinds of studies. Ali et al [10] studied the viscometric and refractive index behaviour of glycine in aqueous diol and found that polarisability increases with increase in CH_2 group in diol. Jani et al [11] studied stability complexes of Fe (II) and Fe (III) with 8-aceto-7-hydroxycoumarinhydrazone by Job's method by keeping metal:ligand ratio is 1:1. Ramteke and Narwade et al [12] studied the stability constants of chloro substituted pyrazoles with 3d series elements in 70 % dioxane-water mixture. Shivraj et al. [13] potentiometrically studied 3-amino-5- methylisoxazole schiff bases and their complexes with 3d series elements in solution. Mishra et al [14] have studied synthesis, structure and properties of a monomeric copper(II) complex with a multidentate pyridylpyrazole ligand. In addition to these other physical properties such as viscosity, refractive index and ultrasonic speed of binary mixtures are studied by many workers. Yadav et al [15] studied molecular interaction between some bromo alkane and non-polar hydrocarbon by refractometry. Our research group has reported the formation constant of Al(III) Cr(III)and Fe(III) complexes with same substituted isoxazoles, isoxazolines and pyrazole. Spectrophotometric Studies on stability constant of chlorosubstituted pyrazoles with Cu (II) Nd (III) and Tb (III) metal ions at 0.1 M Ionic strength have been reported by Ramteke et al. [16]. The pharmaceutical uses of metal complexes have been reported by many workers [17]. Studies on special structural requirement and complexation as a possible mode of pesticidal action have also been reported [18-19]. Activity of thiocynate of titanium as plant growth regulator has been reported [20]. The complexes of rare earth with peptides showed the herbicidal and plant growth regularity activity with wheat and barley plant [21]. Here, we report the study of conditional stability constant of transition metal ion complexes with unsymmetrical Schiff base with Cu(II),Ni(II),Co(II) and Fe(III). Since organic drugs have intense biological activity and since no work is reported on the biological applications of binary complexes of Cu(II), Ni(II) and Co(II) with pure ligand and control solution. To study the effect of complex, ligand and control solution on germination survival, seedling height etc. for *Triticum aestivum* (Wheat) and *Trigunella* (Methi) plants in order to make suggestion whether complex and ligands can be used as plant growth regulators in the present study.

2. EXPERIMENTAL

Unsymmetrical Schiff base ligand H_2L^1 and H_2L^2 have been synthesized in laboratory by standard method [22-23]. The nitrate salt of Cu, Ni, Co, Fe and potassium nitrate were used and their solutions (0.1M) were prepared in distilled water. The solution of potassium nitrate 0.1M was prepared and used maintaining ionic strength constant Systronic spectrophotometer was used for measuring absorption of solution. The solutions of ligand $H_2L^1$and H_2L^2 in different percentage of dioxane-water were prepared. Effect of binary complexes on germination, survival and seedling height of triticum aestivum (wheat) and trigunella (methi) plants are studies for biological study the metal ion used are Cu (II),Ni(II),Co(II)and Fe(III) and ligand $H_2L^1$and H_2L^2 are used in present study. The application of complexes in general is studied by dissolving it in proper solvent at desired pH or it is formed during the reaction. The biological application is therefore studied in aqueous medium at pH 3.0, 7.0 and 9.0 and at constant ionic strength of 0.001 M potassium nitrate solution.



N''- [1- (5-chloro- 2-hydroxyphenyl) ethylidene]-*N'''*-[1-(2-hydroxy-5-methylphenyl) ethylidene] carbonohydrazide (H_2L^1)



N''-[1- (2-hydroxy-5- methyl-3-nitrophenyl) ethylidene]-*N*'''- [1-(2-hydroxy-5-methyl phenyl) ethylidene] carbonohydrazide. (H_2L^2**)**

3. RESULTS AND DISCUSSION

pH-Metric method

The pH-Metric study (fig. 1-8) has been done with a limited aim to compare the formation constant value obtained spectrophotometrically. It could be seen from table 1 that there is good agreement of proton-ligand stability constant between half integral method and pointwise calculation method the pk value for H_2L^2 is found to be greater as compare to ligand H_2L^1.the $\log k_1$ and $\log k_2$ value obtained are found to be good agreement with half integral method and pointwise calculation method that shown in table 1 for each system the pH value at which metal complex formation started and hydrolysis commenced have been tabulated and data are presented in table 2.

Spectrophotometric measurement by Jobs method

The spectrophotometric studies has been done with limited aim of comparing the results obtained by this techniques with those of pH-metric techniques pk and log k value are determined at 0.1M ionic strength which is maintained constant by addition of appropriate amount of 1M potassium nitrate solution (table 3). Equimolar solution of Cu (II),Ni(II),Co(II)and Fe(III) with H_2L^1 and H_2L^2 (1.00×10^{-2}m) were mixed in different ratios to prepare jobs solution final volume of each solution made up to 10ml after adjusting the appropriate pH and maintaining constant ionic strength μ=0.1M.In addition to wavelength of maximum λ_{max} same other wavelength were selected. The absorption for all the composition was recorded at a constant wavelength λ_{max} the data of absorption and percentage composition of metal ion and ligand solution at constant pH can be used and curves were constructed (fig 9-12). It is observed that 1:1 complex formation curves occurs in pH range 4 to5 and 1:2 complex formation in the range of 3 to 6 each solution is diluted up to 15 ml and recorded absorption at same max conditional stability constant of metal-ligand complexes were calculated for all the system using following equation.

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

Conditional stability constants are found to be smaller than real stability constant. The agreement between the values obtained by both techniques is fairly good (table 4).

Agricultural Study

It is clear from table 5 to 10 that, in case of *Triticum aestivum*(Wheat), with creasing the pH value, percentage of germination and percentage of survival increased, but in case of *Trigunella* (Methi), reversed effect was observed with increase the pH value. The percentage germination in all treatments increases for Co(II) complex as compared to rest of the complexes and ligands. From Table 4 to 6 clearly indicate that, root length increases with increasing pH value, but in the Co(II)-H_2L^2 complex the root length decreases with 3increase in the pH value. It could see from Table 1 to 6 that root-soot ratio in all the systems for pH 3.0, 5.0 and 7.0 showed abnormal behaviors which may be due to not orderly germination. The changes in the growth pattern of root and soot were studied by the proportional growth in both the cases. The root and soot ratio reflect the same and represent the development in root and soot simultaneously. It is observed from all table that Co(II)-H_2L^2 complexes showed better plant growth regulators for *Triticum aestivum* (Wheat) and *Trigunella (*Methi) plants.

ACKNOWLEDGMENTS

Authors are thankful to the Principal, NKS Model College, Karanja Ghadge, Dist.-Wardha, India, for providing necessary laboratory facilities.

Table:1

Metal-Ligand Stability Constants by Different Methods

System	Constants	Method	
		Half Integral	**Pointwise**
Fe(III) - Ligand (H_2L^1)	log K_1 log K_2	4.13331 3.2875	3.294476 3.04800
Ni(II) - Ligand (H_2L^1)	log K_1 log K_2	3.80189 2.72865	2.41295 3.83387
Co(II) - Ligand (H_2L^1)	log K_1 log K_2	3.37398 4.14398	4.196672 2.01328
Cu(II) - Ligand (H_2L^1)	log K_1 log K_2	2.381287 3.801724	3.42832 4.362876
Fe(III) - Ligand (H_2L^2)	log K_1 log K_2	2.162897 3.92672	2.2662098 5.484209
Co(II) - Ligand (H_2L^2)	log K_1 log K_2	2.14298 2.161198	2.3151982 2.01209
Cu(II) - Ligand (H_2L^2)	log K_1 log K_2	1.92872 2.582098	2.632912 3.022099
Ni(II) - Ligand (H_2L^2)	log K_1 log K_2	2.42524 1.971290	2.88298 2.602653

Table: 2
Commencement of the hydrolysis and complete formation

Metal Ion	pH at the commencement of the Hydrolysis	pH at the commencement of complete formation
Fe(III)	7.5	6.50
Cu(II)	6.5	5.05
Co(II)	5.0	5.60
Ni(II)	7.0	6.80

Table: 3

Determination of conditional stability of metal-ligand complex by Jobs method

System	Concentration complex (x) mole lit^{-1}	Conditional stability constant (K)	log K
Ni(II) –H_2L_1	1.82857	1.00488	0.01646
Cu(II) –H_2L_1	1.719354	1.22247	0.14329
Ni(II) –H_2L_2	1.26857	1.65256	0.19367
Co(II) –H_2L_2	1.19875	1.19034	0.01061
Co(II) –H_2L_1	1.06198	1.24917	0.03691

Table: 4

Comparison of log K values between pH-metry and spectrophotometry techniques

System	pH-metric log K	Spectrophotometric log K
Cu(II) –H_2L_1	3.29181	2.32182
Ni(II) –H_2L_1	2.18113	2.17622
Co(II) –H_2L_2	1.83718	2.461187

Table: 5

Effect of Ligand and Complexes on Germination and Survival of *Triticum aestivum*) Wheat seed.

Ligand: H_2L^1 $\propto$ = 0.1 M pH = 3.0

Parameters	Effect of			Effect of Complexes with Ligand (H_2L^1)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	28	35	55	35	50	30	Ni(II) > Ligand > Co(II) > Cu(II)
% Survival after 8 days	55	60	62	64	78	64	
Root length (mm)	12.19	17.10	13.00	13.00	18.22	13.54	
Shoot length (mm)	16.94	17.48	19.36	15.20	18.20	15.74	Ni(II) is having an excellent function as a plant growth regulator
Seedling height (mm)	31.98	33.70	31.80	28.20	34.28	30.30	
Root Shoot Ratio	0.452	0.588	0.508	0.516	0.598	0.500	
Leaf Length (mm)	10.28	12.28	16.80	10.34	12.96	10.38	

Acid Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

Ligand Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1+ 30 ml water

Metal Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1+ 2 ml metal ion + 28 ml water.

Table: 6

Effect of Ligand and Complexes on Germination and Survival of (*Triticum aestivum*) Wheat seed.

Ligand : H_2L^1 $\propto = 0.1$ M pH = 5.0

Parameters	**Effect of**			**Effect of Complexes with Ligand** (H_2L^1)			**General order of Plant growth regulator**
	Water	**Ligand**	**Acid**	**Cu(II)**	**Ni(II)**	**Co(II)**	
% Germination after 5 days	43	48	48	62	55	52	Cu(II) > Ni(II) > Co(II) > Ligand
% Survival after 8 days	40	44	52	52.02	56	51	
Root length (mm)	10.02	10.45	10.64	12.40	11.84	12.64	Cu(II) is having an excellent function as a plant growth regulator
Shoot length (mm)	14.12	15.50	16.24	16.38	16.94	17.30	
Seedling height (mm)	25.04	26.28	28.30	30.28	29.48	30.64	
Root Shoot Ratio	0.438	0.504	0.498	0.502	0.538	0.488	
Leaf Length (mm)	10.48	10.30	12.94	12.74	11.38	12.98	

Acid Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

igand Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1+ 30 ml water

Metal Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1+ 2 ml metal ion + 28 ml water

Table: 7

Effect of Ligand and Complexes on Germination and Survival of (*Triticum aestivum*) Wheat seed.

LiganH$_2$L^1 ∝ = 0.1 M pH = 7.0

Parameters ``	Effect of			Effect of Complexes with Ligand (H_2L^1)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	41	44	43	49	73	74	Co(II) > Ni(II) > Cu(II) > Ligand
% Survival after 8 days	53	54	57	59	61	68	
Root length (mm)	9.38	8.08	09.20	9.31	9.90	9.98	Co(II) is having an excellent function as a plant growth regulator
Shoot length (mm)	13.37	10.82	14.08	14.28	15.10	15.44	
Seedling height (mm)	29.30	23.06	25.36	25.29	27.29	26.20	
Root Shoot Ratio	0.548	0.478	0.296	0.298	0386	0.392	
Leaf Length (mm)	13.28	11.86	12.70	13.16	14.20	12.18	

Acid Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

Ligand Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1 + 30 ml water

Metal Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_1 + 2 ml metal ion + 28 ml water

Table: 8

Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed.

Ligand : H_2L^2 $\propto = 0.1$ M pH = 3.0

Parameters	Effect of			Effect of Complexes with Ligand (H_2L^2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	55	65	49	68	64	66	Cu(II) > Co(II) > Ligand > Ni(II)
% Survival after 8 days	58	67	70	82	68	80	
Root length (mm)	5.98	5.28	5.08	6.90	5.48	6.70	Co(II) is having an excellent function as a plant growth regulator
Shoot length (mm)	7.48	6.18	6.98	8.88	7.50	8.60	
Seedling height (mm)	27.08	26.38	26.28	30.86	29.08	30.40	
Root Shoot Ratio	0.208	0.298	0.284	0.326	0.328	0.312	
Leaf Length (mm)	6.88	5.88	5.96	5.44	5.36	5.38	

Acid Solution: - 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

Ligand Solution: - 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2+ 30 ml water

Metal Solution: - 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2 + 2 ml metal ion + 28 ml water

Table: 9

Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed

Ligand : H_2L^2 $\propto$ = 0.1 M pH = 5.0

Parameters	Effect of			Effect of Complexes with Ligand (H_2L^2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 2½ days	38	38	44	52	53	58	Co(II) > Cu(II) > Ni(II) > Ligand
% Survival after 8 days	43	45	51	55	59	63	
Root length (mm)	2.98	2.96	3.08	3.20	3.88	4.18	Co(II) is having an excellent function as a plant growth regulator
Shoot length (mm)	5.20	5.32	5.48	4.80	5.65	5.69	
Seedling height (mm)	24.18	21.08	26.20	26.04	24.12	24.02	
Root Shoot Ratio	0.585	0.590	0.565	0.652	0.629	0.689	
Leaf Length (mm)	6.90	6.18	6.28	6.08	6.30	6.50	

Acid Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

Ligand Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2
+ 30 ml water

Metal Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2
+ 2 ml metal ion + 28 ml water

Table: 10

Effect of Ligand and Complexes on Germination and Survival of (*Trigunella*) Methi seed.

Ligand : H_2L^2 $\propto$ = 0.1 M pH = 7.0

Parameters	Effect of			Effect of Complexes with Ligand (H_2L^2)			General order of Plant growth regulator
	Water	Ligand	Acid	Cu(II)	Ni(II)	Co(II)	
% Germination after 5 days	38	45	46	52	53	57	Co(II) > Ni(II) > Cu(II) > Ligand
% Survival after 8 days	33	38	42	44	52	59	
Root length (mm)	4.98	4.18	4.30	4.22	4.33	4.32	Co(II) is having an excellent function as a plant growth regulator
Shoot length (mm)	3.32	3.08	3.20	3.46	3.40	3.42	
Seedling height (mm)	23.08	20.06	24.02	20.65	25.16	25.58	
Root Shoot Ratio	0.652	0.697	0.729	0.795	0.742	0.760	
Leaf Length (mm)	6.20	6.98	6.80	7.06	6.94	7.64	

Acid Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 40 ml water.

Ligand Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2+ 30 ml water

Metal Solution :- 5 ml HNO_3 (0.1 M) + 5 ml KNO_3 (1 M) + 10 ml ligand H_2L_2+ 2 ml metal ion + 28 ml water

Fig. 1
Ligand - H_2L^1
SYSTEM - Ni(II) - Complex

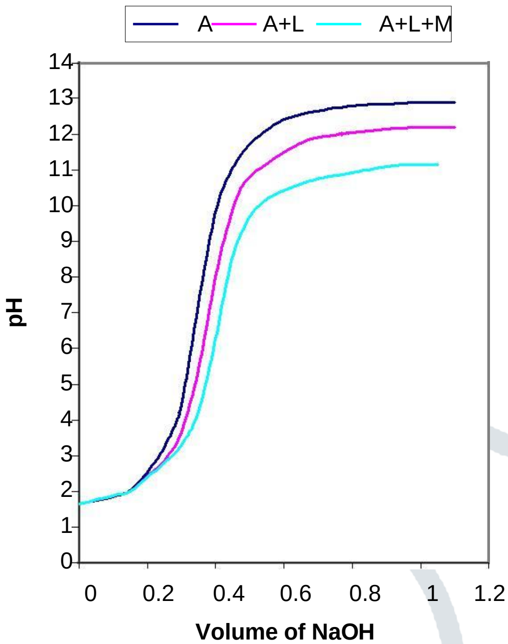


Fig. 2
Ligand - H_2L^1
SYSTEM - Co(II) - Complex

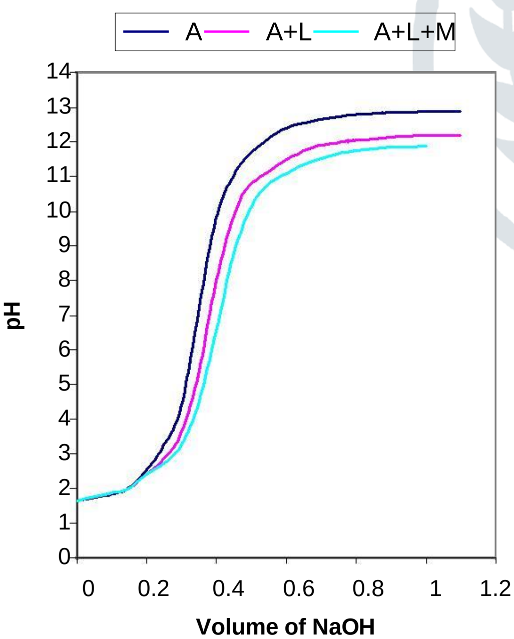


Fig. 3
Ligand - H_2L^1
SYSTEM - Cu(II) - Complex

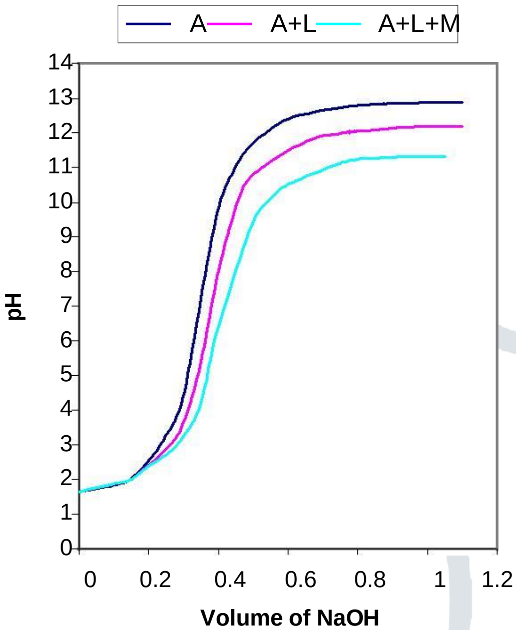


Fig. 4
Ligand - H_2L^1
SYSTEM - Fe(III) - Complex

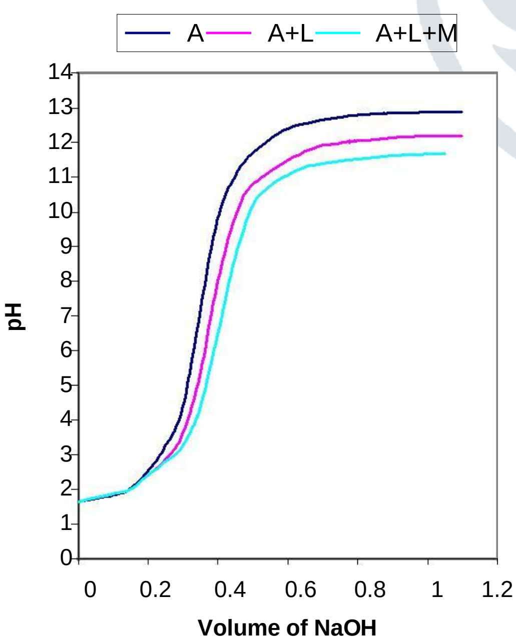


Fig. 5

Ligand - H_2L^2

SYSTEM - Ni(II) - Complex

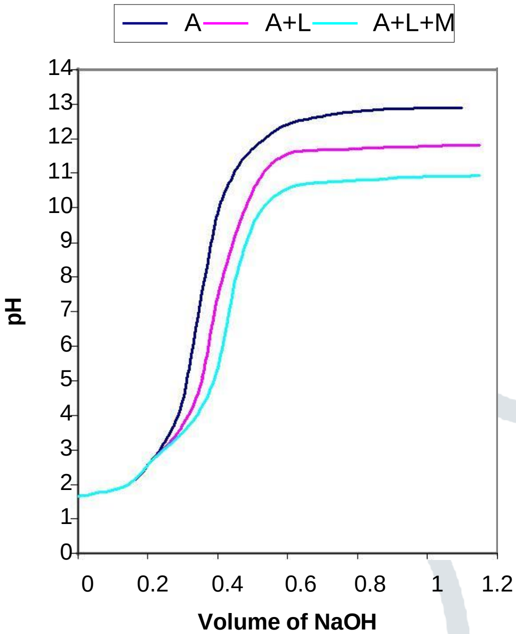


Fig. 6

Ligand - H_2L^2

SYSTEM - Co(II) - Complex

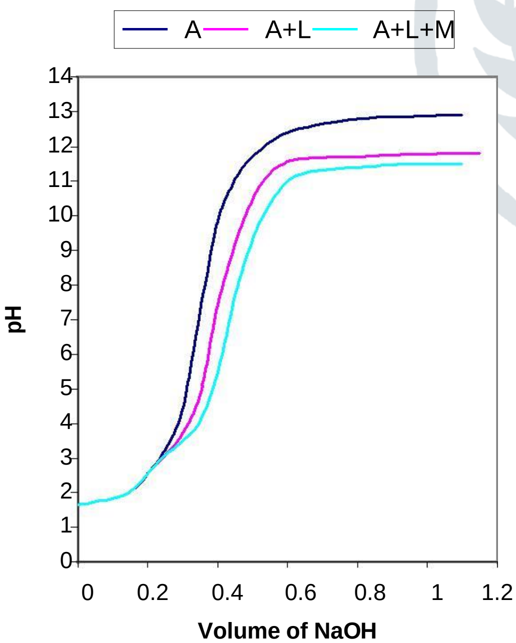


Fig. 7
Ligand - H_2L^2
SYSTEM - Cu(II) - Complex

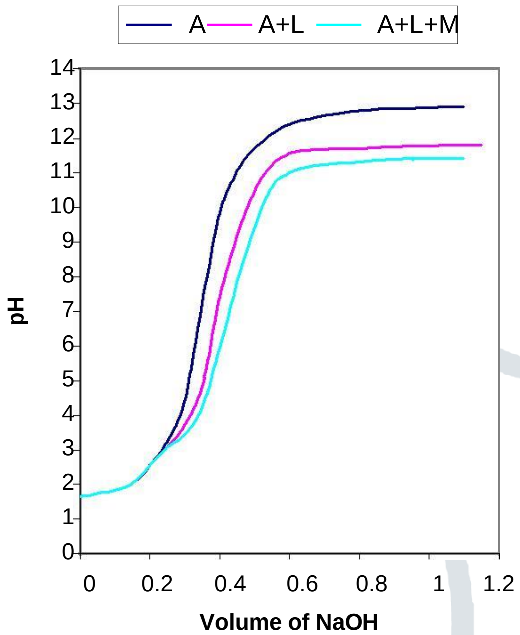


Fig. 8
Ligand - H_2L^2
SYSTEM - Fe(III) - Complex

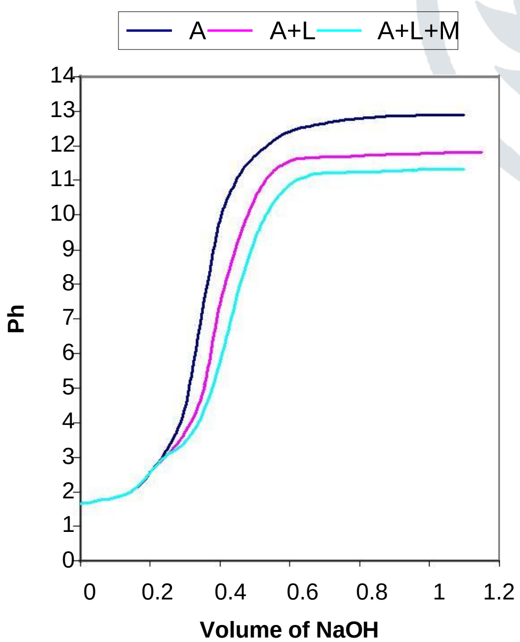


Fig. 9
Job's Variation Method
SYSTEM - Ni(II)-H_2L^1

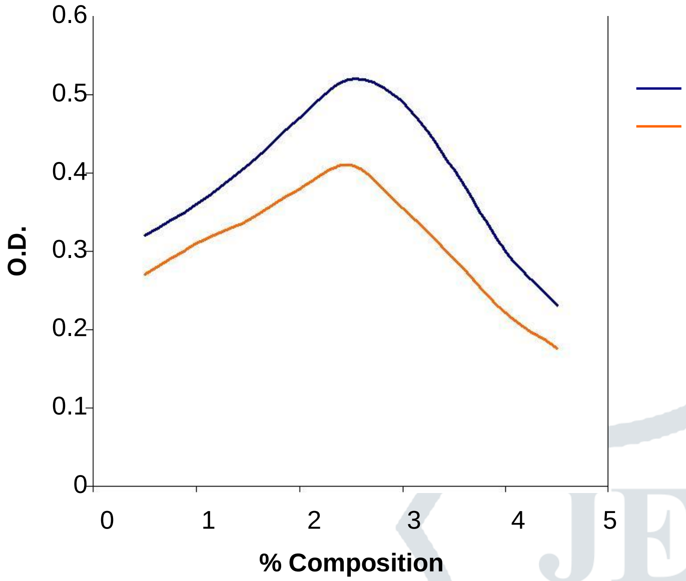


Fig. 10
Job's Variation Method
SYSTEM - Co(II)-H_2L^1

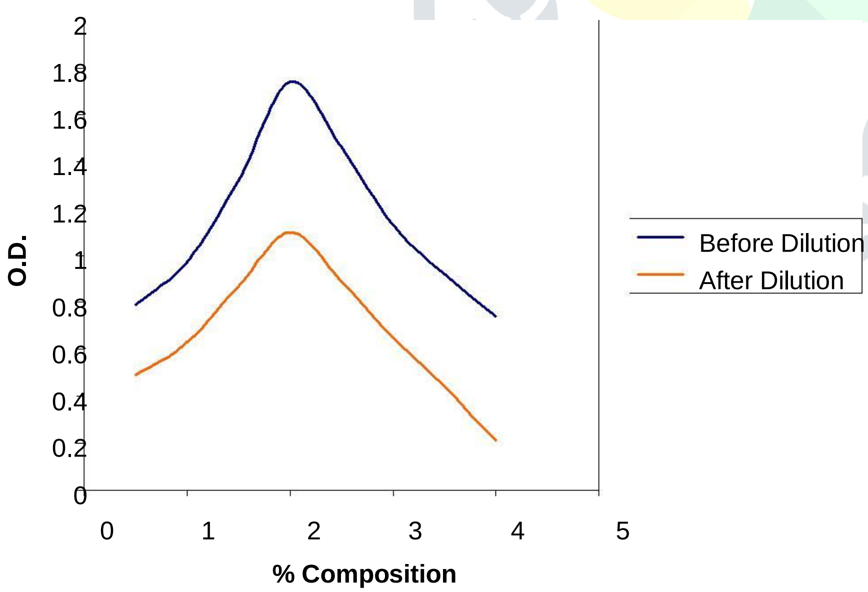


Fig. 11
Job's Variation Method
SYSTEM - Ni(II)-H_2L^2

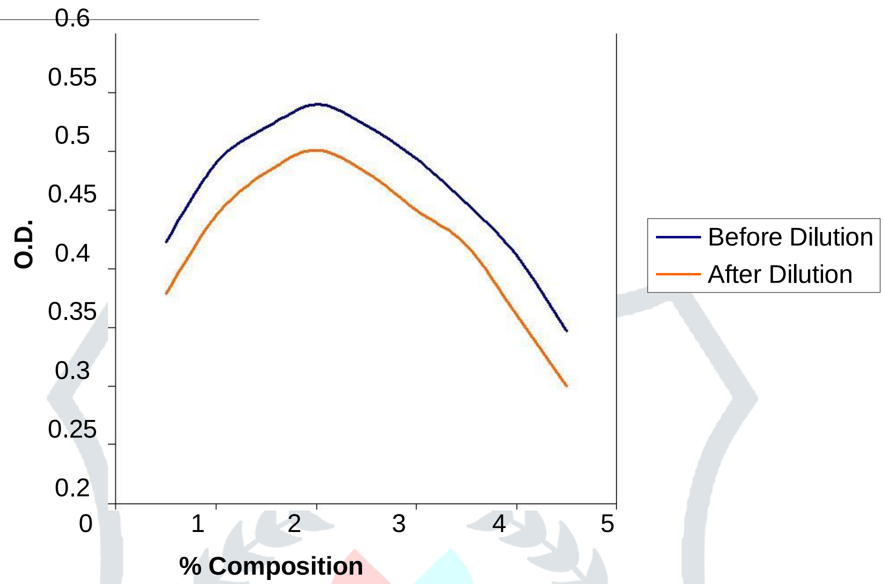
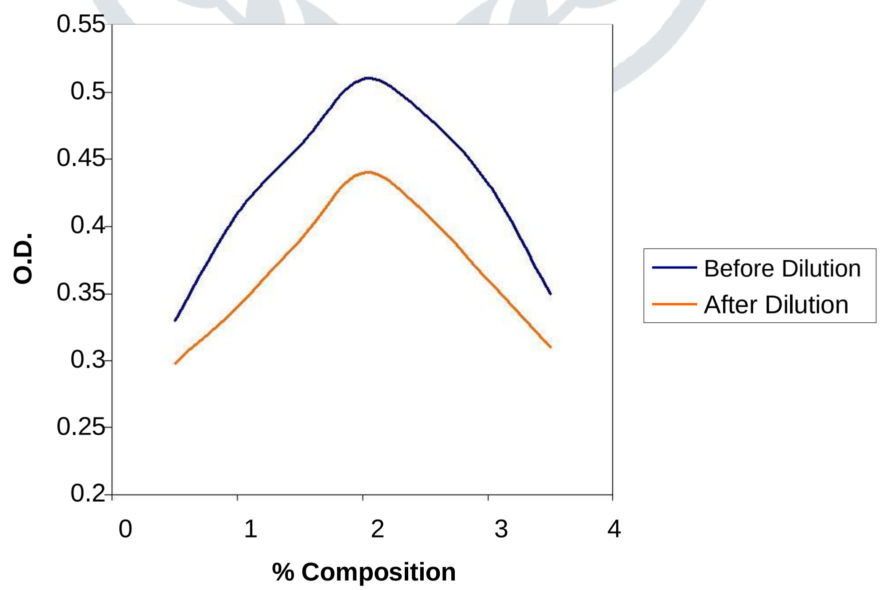


Fig. 12
Job's Variation Method
SYSTEM - Cu(II)-H_2L^2



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