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Spectrophotometric study of complexes to determine the formulae and stability constant

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ABSTRACT

As we know that complexes formation tendency is depends on nature of central metal ions and ligands. Both chemical species responsible for formulae and stability constant during the formation of complexes and ratio of both chemical species shown the composition of formulae and stability constant. Stability constant in solution of both chemical species shown the thermodynamic stability or kinetic stability of complexes. For this purpose, spectrophotometric used to determine the formulae and stability constant of complexes. Spectrophotometric out of which one is the method of continuous variation, which was designed by Job, hence called as job's method. The absorbance of Copper –EDTA Complex, Cobalt –Hydrazine complex, and Zinc – EDTA Complex, determined for each of the above complexes were measured by Systronics UV- Visible Spectrophotometer. In practice an equilibrium solution of the two reactants are mixed in varying ratios and the absorbance of each mixture is determined at a selective wavelength. The absorbance is plotted against the mole fraction of the metal or ligand in the flasks. The resulting curves are called as jobs plots. The ratios that corresponds to the mole fractions the components in the complex will attain a maximum absorbance value. The positions of the maximum indicate the ligand metal ratio of the complex in solution. The value of maxima was the value of 'n' in the formula of the complex, thus one can determine the formula of the complex.

Key words: Formulae and stability constants, mole fraction, UV- Visible Spectrophotometer, ligands, central metal ions.

Introduction:

A number of methods are used to determine the formulae and stability constant of complexes spectrophotometric, out of which one is the method of continuous variation, which was designed by Job, hence called as job's method. The absorbance Copper – EDTA Complex, Cobalt –Hydrazinate complex, and Zinc – EDTA Complex, determined for each of the above complexes were measured by Systronics UV- Visible Spectrophotometer.

The principle of continuous variation was employed by Ostromisslensky in 1911 to establish the 1:1 stoichiometry of the adduct formed between nitrobenzene and aniline. However, the principle was then applied by job in the study of formation of complexes of coordination compounds and hence named after him as jobs method. Job assumed that only one complex is present in solution. The method is also described in another way which is also applicable for determining the molecular formulae of complexes, spectrophotometric, that one produced as products of incomplete equilibrium reactions.

In practice an equilibrium solution of the two reactants are mixed in varying ratios and

the absorbance of each mixture is determined at a selective wavelength. The absorbance is plotted against the mole fraction of the metal or ligand in the flasks. The resulting curves are called as jobs plots. The ratios that corresponds to the mole fractions the components in the complex will attain a maximum absorbance value. The positions of the maximum indicate the ligand: metal ratio of the complex in solution. For eg. a maximum corresponding to 0.5 on the mole fraction ratio of the ligand scale shows a complex of 1:1 composition, while maximum at 0.67 and 0.75 indicates complexes of 2:1 & 3:1 ligand: Metal ratios respectively. The value of maxima is the value of 'n' in the formula of the complex, thus one can determine the formula of the complex.

Methodology:

In this study we used job's method of variation to study the ratio of metal ion and ligand in certain complexes for this purpose. In experimental study the five different complexes were performed. Absorbance for each of the above complexes were measured by Systronics UV- Visible Spectrophotometer.

1. Copper –EDTA Complex

2. Cobalt –Hydrazinate complex
3. Zinc – EDTA Complex

Copper (II) – EDTA Complex

1. 0.005M solution of $CuSO_4.5H_2O$ by dissolving 0.4653 gms in 250ml of distilled water. Similarly, 0.005M solution of EDTA was prepared. Instrument was standardized using water as reference to measure absorbance as zero at the wavelength of 740 nm. In a beaker 3 ml of $CuSO_4$ and 27 ml of EDTA solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 740nm. Similarly, absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $CuSO_4$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

$$XL = V_L / V_L + V^{o}_{M}$$

Where V_L - is the volume of the titrant added at each V^{o} - is the initial volume of metal titrant. 15/30 = 0.5 M

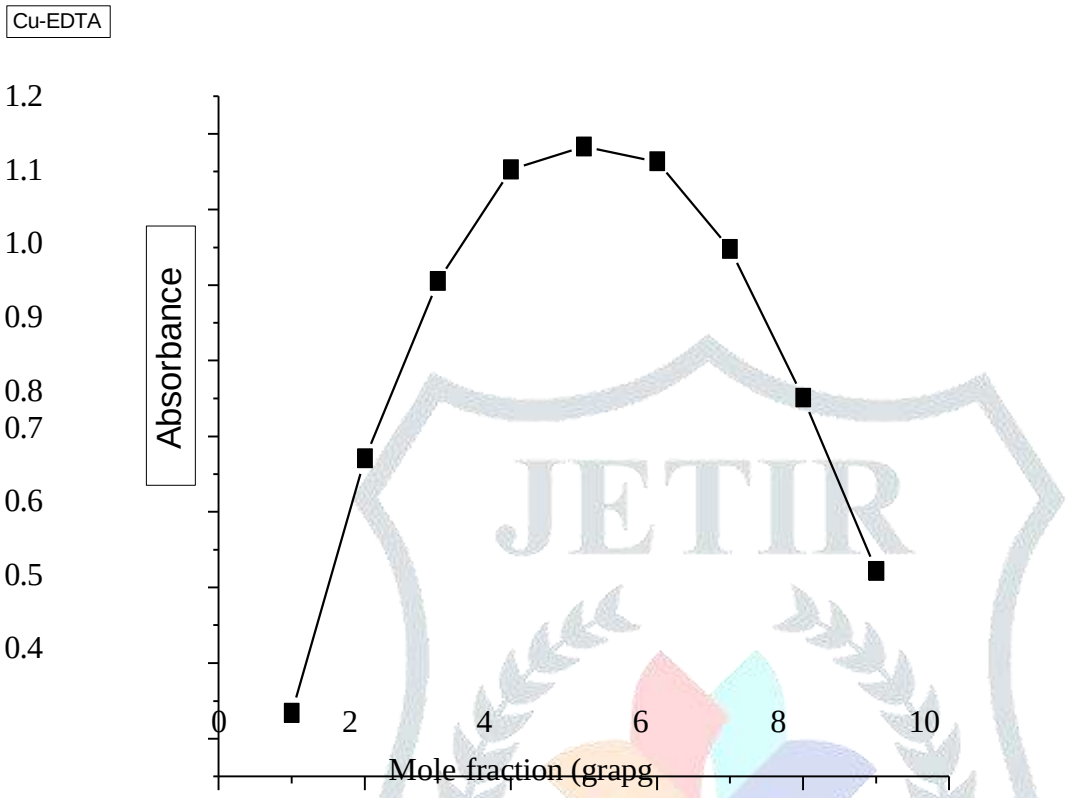
The value of n = 0.5 indicates that in the $CuSO_4.5H_2O$ & EDTA complex the metal to ligand ratio is 1:1.

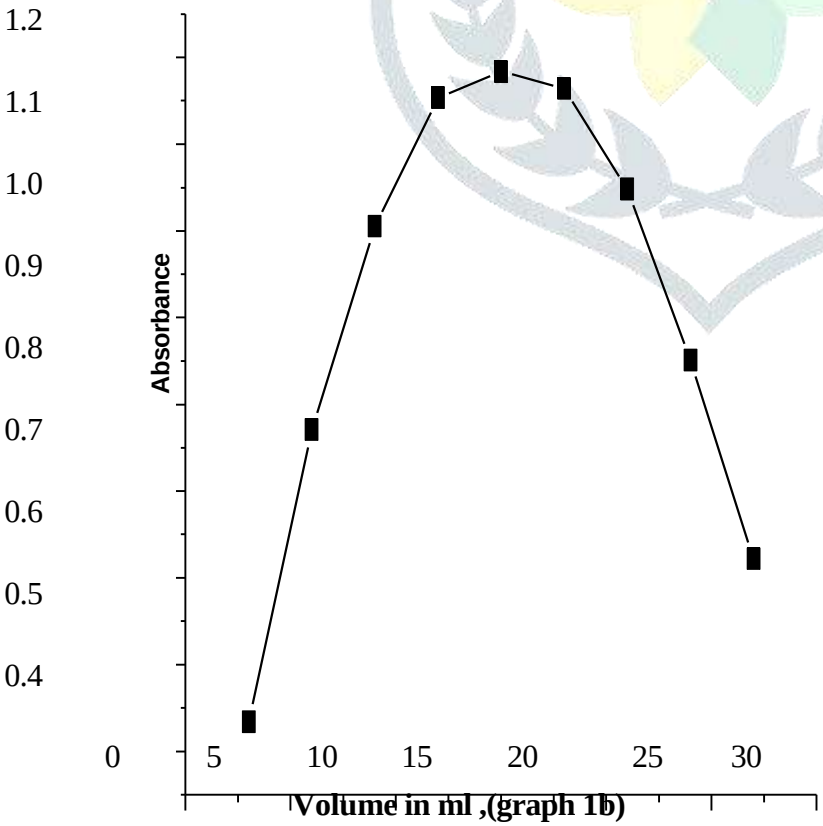
The graph 1a & 1b shows the photometric curve at 740 nm by titrating solution A with solution B, the graphs are given below

Observation Table -1

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.4339	0.9
6	24	0.7713	0.8
9	21	1.0051	0.7
12	18	1.1532	0.6
15	15	1.1836	0.5

18	12	1.1639	0.4
21	9	1.0481	0.3
24	6	0.8512	0.2
27	3	0.6219	0.1





Cobalt – Hydrazinate complex:

2. 0.005M solution of $CoCl_2.6H_2O$ by dissolving 0.2967 gms in 250ml of distilled

water. Similarly, 0.005M solution of NH_2. $NH_2.H_2O$ was prepared. Instrument was standardized using water as reference to measure absorbance as zero at the wavelength of 635 nm. In a beaker 3 ml of $CoCl_2.6H_2O$ and 27 ml of NH_2. $NH_2.H_2O$ solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 635nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $CoCl_2.6H_2O$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

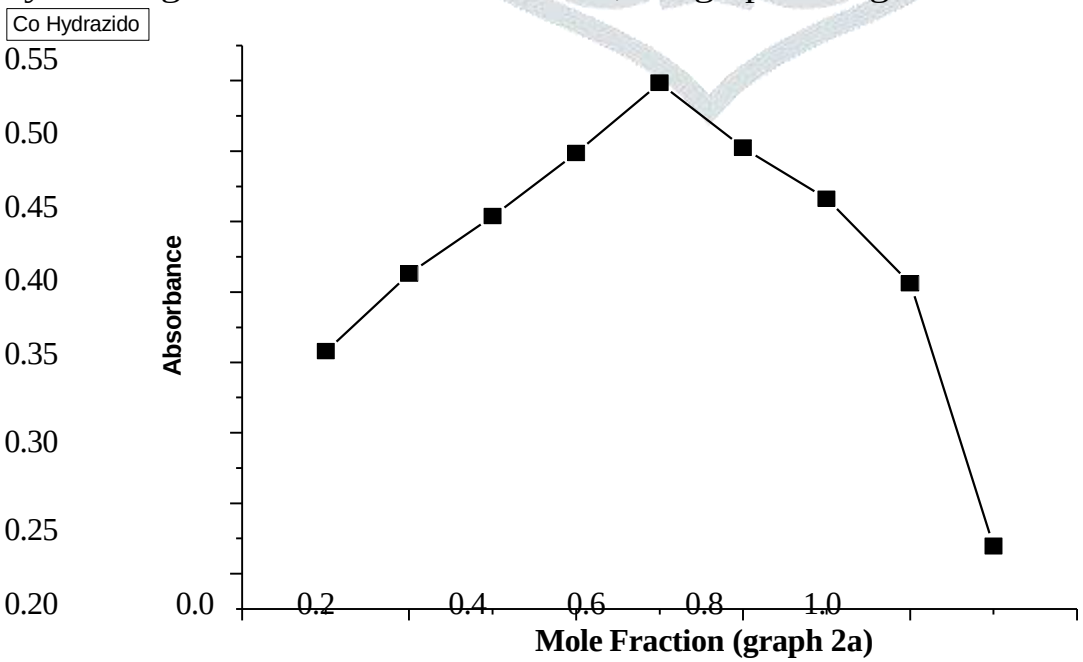
$$XL = V_L / V_L + V^{o}_{M}$$

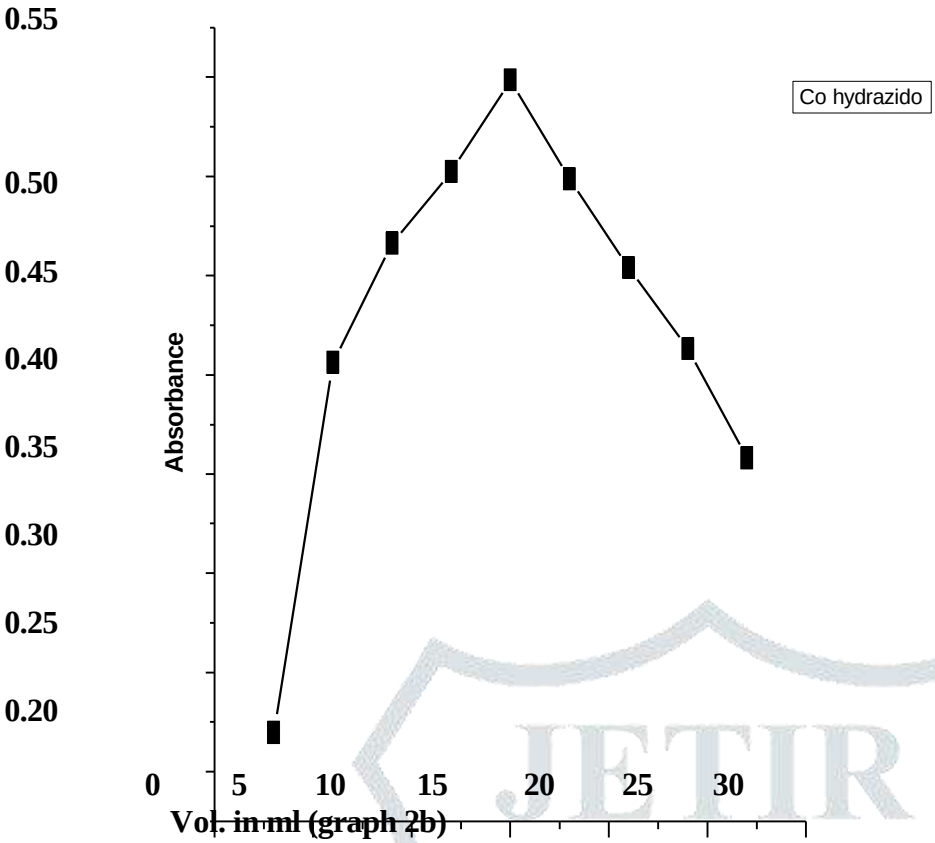
Where V_L - is the volume of the titrant added at each V^{o} - is the initial volume of metal titrant. 15/30 = 0.5 M

Observation Table-2

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactant s
3	27	0.2199	0.9
6	24	0.4062	0.8
9	21	0.4662	0.7
12	18	0.5022	0.6
15	15	0.5486	0.5
18	12	0.4987	0.4
21	9	0.4540	0.3
24	6	0.4132	0.2
27	3	0.3581	0.1

The value of n = 0.5 indicates that in the $CoCl_2.6H_2O$ & NH_2. $NH_2.H_2O$ complex the metal to ligand ratio is 1:1.The graph 2a & 2b shows the photometric curve at 635nm by titrating solution A with solution B, the graphs are given below.





Zn – EDTA Complex

3. 0.005M solution of $ZnSO_4$.$7H_2O$ by dissolving 0.3344 gms in 250ml of distilled water. Similarly 0.005M solution of EDTA was prepared. Instrument was standardized using water as reference to measure absorbance as zero at the wavelength of 240 nm. In a beaker 3 ml of $ZnSO_4$ and 27 ml of EDTA solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 740nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $ZnSO_4$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

Complex the metal to ligand ratio is 1:1.The graph 3a & 3b shows the photometric curve at 645nm by titrating solution A with solution B, the graphs are given below.

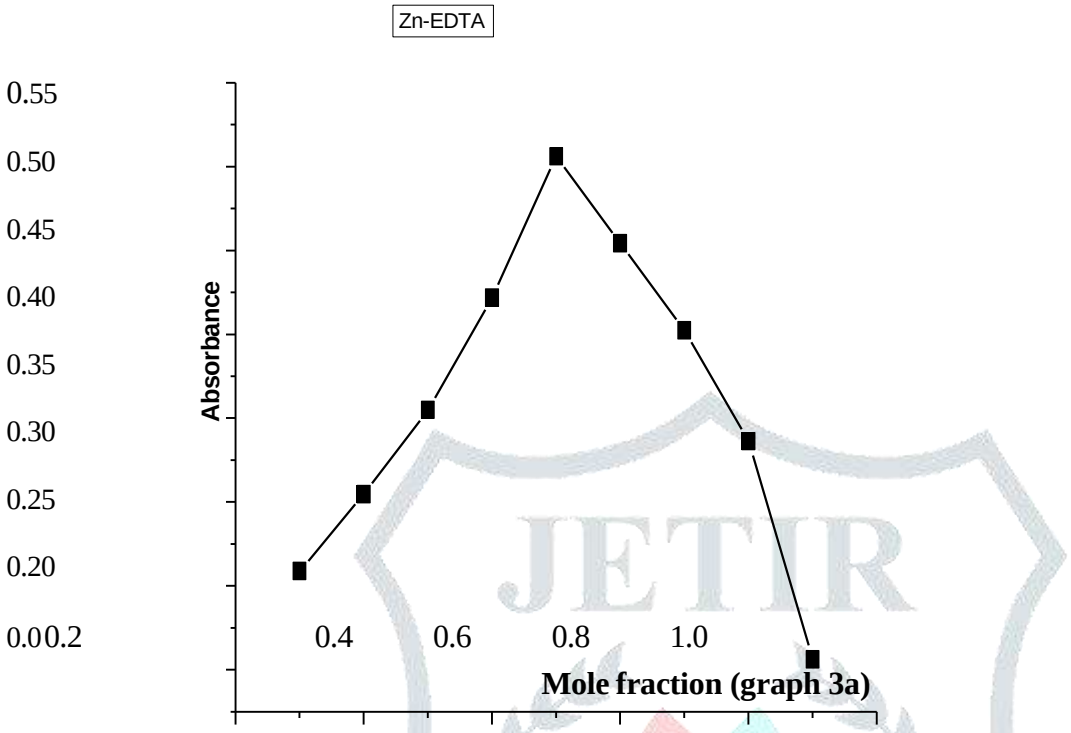
$$XL = V_L / V_L + V^{o}_{M}$$

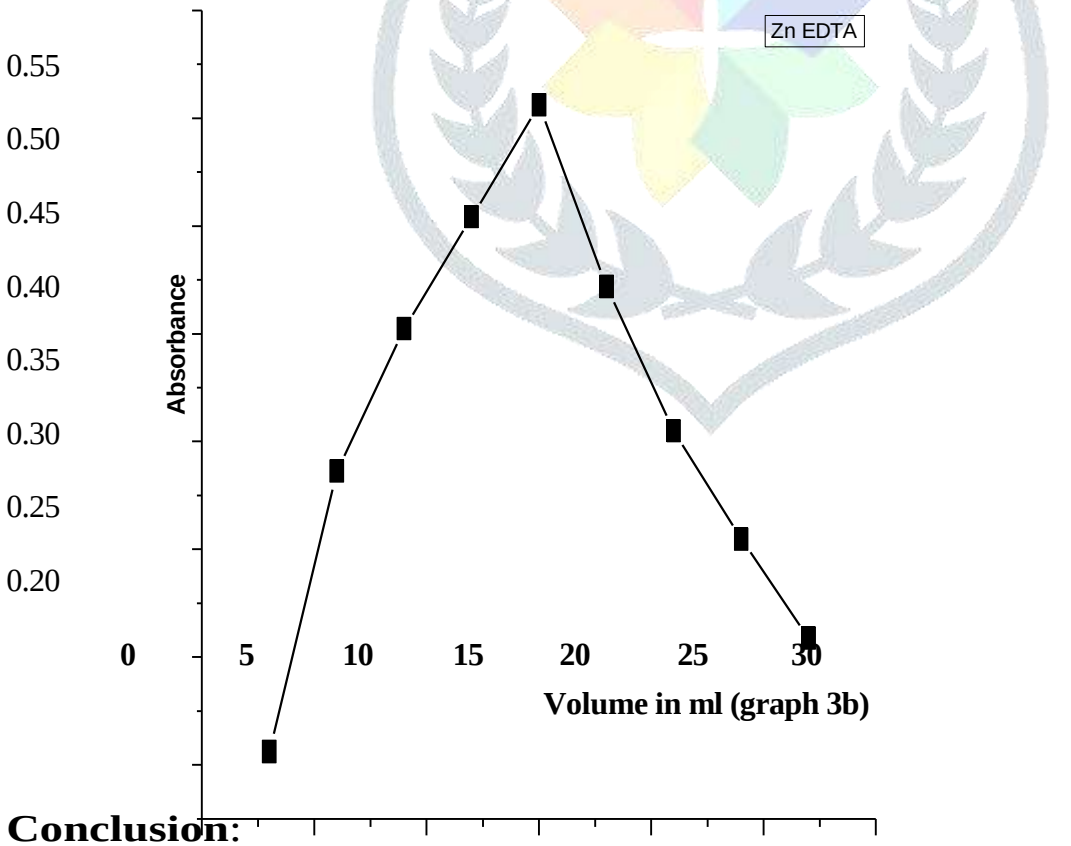
Where V_L - is the volume of the titrant added at each V^{o} - is the initial volume of metal titrant.15/30 = 0.5 M

Observation Table-3

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactant s
3	27	0.2061	0.9
6	24	0.3362	0.8
9	21	0.4024	0.7
12	18	0.4543	0.6
15	15	0.5061	0.5
18	12	0.4220	0.4

21	9	0.3549	0.3
24	6	0.3047	0.2
27	3	0.2589	0.1





Conclusion:

1. Since the plot exhibit at XCu^{2+}= 0.5, it indicates the formulation of 1:1 complex
2. Since the plot exhibit at X Co^{2+}= 0.5, it indicates the formulation of 1:1 complex.
3. Since the plot exhibit at XZn^{2+}= 0.5, it indicates the formulation of 1:1 complex.

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