

Spectrophotometric Determination of Composition and Formation Constant, And Computation of Thermodynamic Parameters – ΔG^0 , ΔH^0 & ΔS^0 for Complexation Process Between Rubidium Acetyl Salicylate and N,N'-1,2-Ethylenebis(Ortho-hydroxyacetophenoniminato) Copper(II) Forming Hetero-Binuclear Complex in Acetone

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Abstract: Spectrophotometric techniques are used as a tool for determining composition (Stoichiometry) as well as metal-ligand stability constant (formation constant) of metal complexes. In the present studies, composition of a hetero binuclear complex synthesized from complexation between Rubidium Acetyl Salicylate and N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) Copper(II) [CuEohacp] and metal-ligand formation constant (stability constant) of the metal complex [CuEohacpRbAp] using acetone as solvent, has been determined using light absorption measurement data obtained from spectrophotometry. This goal has been accomplished by adopting Job's method of continuous variation and earlier reported mathematical evaluation process. The composition of the resulting metal complex obtained by the complexation between Rubidium Acetyl Salicylate and N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) Copper(II) is found to be Metal : Ligand = 1 : 1. The metal-ligand stability constant of this metal complex at two temperatures, 288K and 301K, is 1.76×10^5 l.mole⁻¹ and 1.05×10^5 l.mole⁻¹ respectively. From these data, thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 of the complexation process in acetone have been evaluated and reported. The results reveal that complexation process is spontaneous at ordinary temperatures, exothermic, and entropically favourable. hetero-binuclear complex [CuEohacpRbAp] is highly stable at ordinary temperatures, and copper (II) complex of Schiff base [CuEohacp] is a good chelating agent.

Keywords: Spectrophotometric techniques, Metal-ligand stability constant, Formation constant, Hetero-binuclear complex, Thermodynamic parameters

I. INTRODUCTION

Wide applicability of coordination compounds in diverse fields of modern life and industrialisation age, coordination compounds have become a very important class of compounds [1-8]. Every year thousands of coordination compounds



are synthesized and added in the list. However, with synthesis knowledge of stability of the metal complexes in different conditions becomes equally important. Stability of a metal complex means it can exist without any type of change, and has a considerable shelf life period [9]. Metal complexes also play various key roles in biological systems. These factors make essential a thorough study of coordination compounds including its stability in various conditions. Formation constant or Stability constant of a metal complex is a measure of its thermodynamic stability. Being complexation process a reversible one, equilibrium constant for metal complex formation is an effective measure of the affinity of a ligand for metal ion in solution and is termed as Formation constant or Stability constant of the metal complex. A general representation of metal complex formation reaction in solution may be considered as:



The overall thermodynamic equilibrium constant is given by:

$$K = \frac{[M_mN_n]_{eq}}{[M]_{eq}^m \cdot [N]_{eq}^n}$$

Where temperature and ionic strength are kept constant.

This overall thermodynamic equilibrium constant is known as Formation constant or Stability constant of the metal complex (K_f).

The stability constant of a metal-ligand complex (K_f or β) is determined using several experimental and graphical methods such as Potentiometric / pH-Metric Method, Spectrophotometric Method, Bjerrum's Half-Value Method, Ion Exchange Method, Polarographic Method, Ion chromatography (IC) hyphenated to inductively coupled plasma mass spectrometry (ICP-MS) method, Conductometric method, etc. M. Wacker and A. Seubert, have reported a method for determination of stability constant of complexation reaction between N,N,N',N' -ethylenediamine tetra acetic acid as ligand and trivalent ions of chromium, iron, gallium, indium, and scandium, based on the addition of a second metal ion as a competitor [10]. A competition approach delivers the ratio of the stability constants of the two competing metal ions. The different species were separated via anion and cation ion exchange chromatography and their metal content was quantitatively detected online utilizing inductively coupled plasma atomic emission spectrometry. Gouda et. al. has determined acid dissociation and complex stability constants of 2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) phenol (H_2A) with metal ions Re^{5+} , Ce^{3+} , Pd^{2+} , Th^{4+} , Hg^{2+} , and Co^{2+} potentiometrically using 0.1 M KCl and 20% (v/v) ethanol-water mixture. They also calculated thermodynamic parameters - ΔG , ΔH and ΔS of the complexation reaction [11]. Choudhari et. al. has reported determination of Stability constant of the complexes of metal ion Fe (III), Mn (II) and Cr (III) with some substituted 2-oxo-2H-chromene-3-carbohydrazide derivatives at 0.1 M ionic Strength at 42°C using the Bjerrum-Calvin titration technique as modified by Irving and Rossotti [12]. Serap Karaderi et. al. has reported about the determination of the Stability Constants of complexes from Metformin Hydrochloride with Cu (II), Cd (II) and Zn (II) potentiometrically [13]. C. Huang and D. Beauchemin have determined the conditional stability constant, K'_f , using ion chromatography (IC) hyphenated to inductively coupled plasma mass spectrometry (ICP-MS) [14, 15]. The voltammetry oxidation peaks for anions and other ligands that react at the Hg electrode was used by George W Luther III, Stephen M Theberge and David Rickard [16] for the determination of stability constants of metal-ligand complexes using the DeFord and Hume formalism. Metal-ligand complexes with known stability constants that span the range of $\log \beta = 2.9-5.9$ were determined using the oxidation wave of the ligand as metal was varied. Ahmed Zain A. Thabet, Mohammad Mohsin, Fahd Saleh T. Saleh and Mohamad Asif have determined the stability constant of coordination complexes of metformin, i.e., 1,1- Dimethyl guanidine hydrochlorides with metals such as Sm^{+2} , La^{+3} , Cu^{+2} , and Mn^{+2} potentiometrically in the presence of $NaClO_4$ at $(27 \pm 0.5)^\circ C$. The findings revealed that the sequence of the stabilization constant of the formal complexes increased from La to Cu as $La < Sm < Mn < Cu$ [17].

In the present study, complexation reaction has been carried out between Rubidium acetyl salicylate (RbAp) and N,N' -1,2- ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) [$CuEohacp$] as ligand forming hetero-binuclear complex [$CuEohacpRbAp$] in acetone. Hence, the complexation reaction may be represented as:



Where n = coordination number of the metal complex.

The metal-ligand formation constant or stability constant of the hetero-binuclear complex [CuEohacpRbAp] in acetone is given by:

$$K_f = \frac{[ML_n]_{eq}}{[M]_{eq} \cdot [L]_{eq}^n}$$

Thus, by putting the values of $[M]_{eq}$, $[L]_{eq}$ and $[ML_n]_{eq}$ the value of stability constant, K_f of the complex, ML_n is computed.

Among the various methods, Spectrophotometric method has been used to determine the composition of the metal complex, and metal-ligand stability constant of the complex. From the results obtained thermodynamic parameters – ΔG^0 , ΔH^0 & ΔS^0 for the complexation process, has been computed. The composition of the metal complex has been established spectrophotometrically using Yoe-Jones method (Mole ratio method). It is found from the experimental results that there is one ligand per metal atom, i.e., Metal:Ligand = 1:1. Using M.C.Chattopadhyaya et al evaluation method [18] for a 1 : 1 metal complex, the formation constant, K_f has been calculated using the following equations:

$$K_f = \frac{[ML]_{eq}}{([M]^0 - [ML]_{eq})([L]^0 - [ML]_{eq})} \quad \dots\dots (i)$$

$$A_{eq} = ([M]^0 - [ML]_{eq}) \cdot \epsilon_M + [ML]_{eq} \cdot \epsilon_{ML} + ([L]^0 - [ML]_{eq}) \cdot \epsilon_L \quad \dots\dots (ii)$$

$$\left(\frac{[M]_1^0 [L]_1^0}{A_1} - \frac{[M]_2^0 [L]_2^0}{A_2} \right) \cdot \epsilon_{ML}^2 + ([M]_2^0 + [L]_2^0 - [M]_1^0 - [L]_1^0) \cdot \epsilon_{ML} + (A_1 - A_2) = 0 \quad \dots\dots\dots (iii)$$

Where $[M]_1^0$, $[L]_1^0$ and $[M]_2^0$, $[L]_2^0$ represent two different concentrations of M and L.

ϵ_M , ϵ_L and ϵ_{ML} are molar attenuation co-efficient of M, L and ML, respectively.

$[M]^0$ and $[L]^0$ are initial molar concentrations of M and L, respectively.

Stability constant of the metal complex has been calculated for two temperatures 288K and 301K and the results obtained as

$$(K_f)_{288} = 1.76 \times 10^5 \text{ l. mole}^{-1}$$

$$(K_f)_{301} = 1.05 \times 10^5 \text{ l. mole}^{-1}$$

Thermodynamic parameters - ΔG^0 , ΔH^0 and ΔS^0 for the complexation reaction between Rubidium acetyl salicylate (RbAp) and N,N'-1,2- ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) [CuEohacp] as ligand forming hetero-binuclear complex [CuEohacpRbAp] in acetone, have been calculated. The high value of formation constant indicates that hetero-binuclear complex [CuEohacpRbAp] is highly stable at ordinary temperatures, and copper (II) complex of Schiff base [CuEohacp] is a good chelating agent.

II. MATERIALS AND METHODS

2.1 Materials and Instrumentation

All chemicals used in the present research work were of A. R. Grade. Systronics UV – Visible Spectrophotometer 117 of 200 – 800nm range was used with 1 cm path length cell for recording absorbance of the experimental samples.

2.2 Methods

2.2.1 Preparation of Rubidium acetyl salicylate (RbAp):

Two equimolar solutions were prepared – one of acetyl salicylic acid (ASPIRIN) in 50% (V/V) aqueous ethanolic solvent and another of Rubidium hydroxide in water. In the first solution second solution was added slowly with



continuous stirring. The resulting solution was concentrated and allowed to crystallize. White flake-like crystals of Rubidium acetyl salicylate appeared. Filtered and washed with water. Recrystallization was completed using ethanol solvent.

2.2.2 Preparation of N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) [CuEohacp]:

In ethanol, liquid o-hydroxyacetophenone was taken and in this solution ethylenediamine was added drop by drop with continuous stirring keeping molar ratio of the two compounds 2:1, respectively. Deep yellow coloured solid Schiff base, N,N'-ethylenebis(ortho-hydroxyacetophenonimine) precipitated out. Precipitate was washed with little ethanol, dried and stored in desiccator over anhydrous CaCl_2 . Ethanolic solution of this Schiff base was added in the ethanolic solution of cupric acetate monohydrate with constant stirring. The resulting solution was warmed below 40°C for 20-25 minutes. Crystalline solid of N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato)copper(II) [CuEohacp] was precipitated out. Precipitate was filtered, washed with little ethanol, dried and kept in desiccator over anhydrous CaCl_2 .

2.2.3 Synthesis of hetero binuclear complex [CuEohacpRbAp] from Rubidium acetyl salicylate and Schiff base N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) copper(II):

Ethanolic solutions of N, N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) and Rubidium acetyl salicylate were mixed together and refluxed for 30 minutes at about $40-50^\circ\text{C}$ and cooled to ice temperature when the complex was separated out. Precipitate was filtered and washed with little ethanol and dried. Finally, the synthesized complex was kept in a desiccator over anhydrous CaCl_2 .

2.2.4 Preparation of standard stock solutions:

10^{-4}M [CuEohacp] solution in acetone

10^{-4}M RbAp solution in acetone

10^{-4}M [CuEohacpRbAp] in acetone

2.2.5 Before determination of stability constant of the metal complex spectrophotometrically, stoichiometry of the species, i.e., number of ligand groups attached to the metal ion has been ascertained by adopting Mole ratio method (Yoe-Jones method). Following working samples were prepared from Rubidium acetyl salicylate (hereinafter, referred by M), N,N'-1,2-ethylenebis(ortho-hydroxyacetophenoniminato) copper(II) (hereinafter, referred by L) and hetero-binuclear complex (hereinafter, referred by ML):

An equilibrated mixture of M and L in acetone having equimolar concentration of $3.33 \times 10^{-5}\text{M}$

An equilibrated mixture of M and L in acetone having equimolar concentration of $1.0 \times 10^{-5}\text{M}$

Separate mixtures in which same volume of stock solution of L was taken with varying volume of stock solution of M and making the resulting solution a definite volume by adding solvent acetone. Resulting solutions were equilibrated for 30 minutes to ensure that equilibrium was established.

Stock solution of ML was scanned between 200 – 800nm at the difference of 10nm and λ_{max} was obtained as 381 nm. This λ_{max} of ML (381 nm) was set as analytical wavelength for all spectrophotometric measurements. All absorption measurements were corrected for solvent and other factors. Absorbance were recorded of samples containing stock solution of M [TABLE – 1], stock solution of L [TABLE – 1], equilibrated mixture of M and L in acetone having equimolar concentration of $3.33 \times 10^{-5}\text{M}$ [TABLE – 2], equilibrated mixture of M and L in acetone having equimolar concentration of $1.0 \times 10^{-5}\text{M}$ [TABLE – 2] and samples of separate mixtures in which same volume of stock solution of L was taken with varying volume of stock solution of M and making the resulting solution a definite volume by adding solvent acetone as prescribed under 2.2.5 (3) [TABLE – 3]. All spectrophotometric measurements of these samples were recorded at two temperatures 288K and 301K.



III. EXPERIMENTAL RESULTS

TABLE – 1

Sample	288 K		301 K	
	Absorbance	ϵ (l.mole ⁻¹ .cm ⁻¹)	Absorbance	ϵ (l.mole ⁻¹ .cm ⁻¹)
10 ⁻⁴ mole.l ⁻¹ M solution	0.032	$\epsilon_M = 3.2 \times 10^2$	0.032	$\epsilon_M = 3.2 \times 10^2$
10 ⁻⁴ mole.l ⁻¹ L solution	2.665	$\epsilon_L = 2.665 \times 10^4$	2.665	$\epsilon_L = 2.665 \times 10^4$

TABLE – 2

Volume of L (ml)	Volume of M (ml)	Volume of acetone (ml)	Resulting Volume (ml)	[M] = [L] in resulting solution (mole.l ⁻¹)	Corrected Absorbance	
					288K	301K
5	5	5	15	3.3 X 10 ⁻³	0.758	0.729
1	1	8	10	1.0 X 10 ⁻³	0.288	0.277

TABLE – 3

Volume of L (ml)	Volume of M (ml)	Volume of acetone (ml)	Resulting Volume (ml)	Corrected Absorbance	
				288K	301K
5	3.0	7.0	15	0.915	0.918
5	3.5	6.5	15	0.882	0.871
5	4.0	6.0	15	0.846	0.825
5	4.5	5.5	15	0.790	0.782
5	5.0	5.0	15	0.758	0.729
5	5.5	4.5	15	0.702	0.691
5	6.0	4.0	15	0.675	0.708
5	6.5	3.5	15	0.683	0.745
5	7.0	3.0	15	0.710	0.782
5	7.5	2.5	15	0.763	0.819
5	8.0	2.0	15	0.825	0.852
5	8.5	1.5	15	0.866	0.887
5	9.0	1.0	15	0.925	0.927

IV. GRAPHICAL AND MATHEMATICAL TREATMENT

Graphs have been plotted between Absorbance (Corrected) and volume of the variant (M) from the data in TABLE – 3 for the temperatures 288K and 301K.



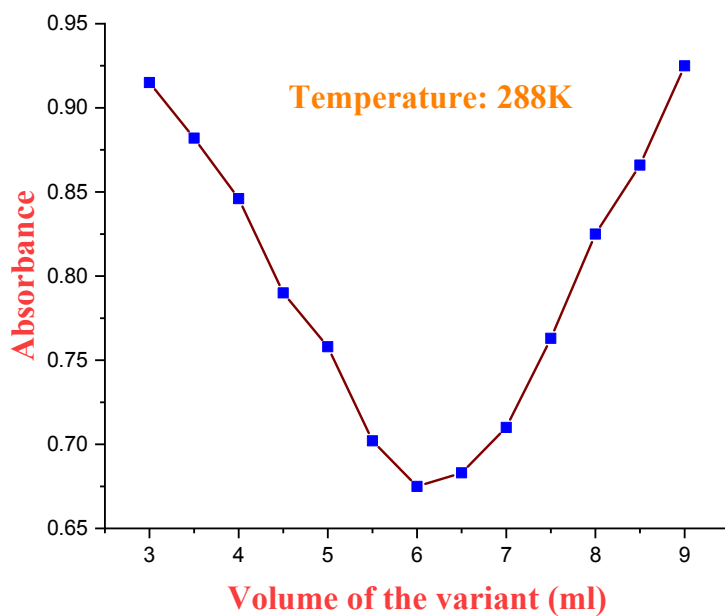


FIGURE. 1: Plot of Absorbance Vs Volume of the variant (M) at 288K

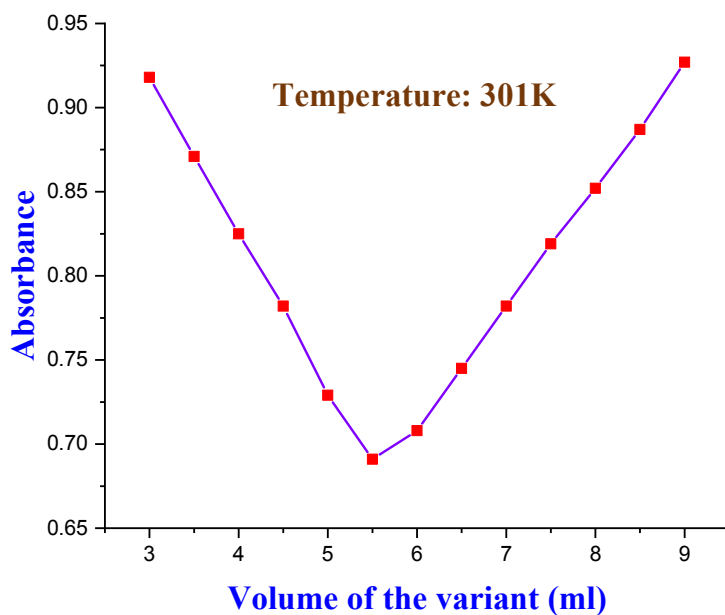


FIGURE.2: Plot of Absorbance Vs Volume of the variant (M) at 301K



Experimentation at temperature 288K

From the graph at FIGURE.1: At the point of break in the slope of the curve

$(V_L)^0 = 5\text{ml}$, $(V_M)^0 = 6.1\text{ml}$, and $A_{eq} = 0.662$

$$\frac{(V_M)^0}{(V_L)^0} = \frac{x_M}{x_L} = \frac{6.1}{5} = 1.22$$

Metal : Ligand = 1 : 1

Thus, the above plot predicts one ligand per metal as the composition of the metal complex.

There-fore, formula of the metal complex is ML .

Putting values $[M]_1^0 = [L]_1^0 = 3.3 \times 10^{-5} \text{ mole.l}^{-1}$,

$[M]_2^0 = [L]_2^0 = 1.0 \times 10^{-5} \text{ mole.l}^{-1}$,

$A_1 = 0.758$, $A_2 = 0.288$

in equation (iii)

$$\left(\frac{[M]_1^0 [L]_1^0}{A_1} - \frac{[M]_2^0 [L]_2^0}{A_2} \right) \epsilon_{ML}^2 + ([M]_2^0 + [L]_2^0 - [M]_1^0 - [L]_1^0) \epsilon_{ML} + (A_1 - A_2) = 0$$

we get, $\epsilon_{ML} = 2.49 \times 10^4$ or 1.73×10^4

Putting $\epsilon_M = 3.2 \times 10^2$, $\epsilon_L = 2.665 \times 10^4$, $A_{eq} = 0.662$, $[M]^0 = 4.06 \times 10^{-5} \text{ mole.l}^{-1}$, $[L]^0 = 3.33 \times 10^{-5} \text{ mole.l}^{-1}$ and taking each value of ϵ_{ML} in equation (ii), $[ML]_{eq}$ has been calculated.

Taking $\epsilon_{ML} = 2.49 \times 10^4$ we get $[ML]_{eq} = 1.15 \times 10^{-4} \text{ mole.l}^{-1}$ which is not acceptable.

Taking $\epsilon_{ML} = 1.73 \times 10^4$ we get $[ML]_{eq} = 2.46 \times 10^{-5} \text{ mole.l}^{-1}$ which is acceptable.

Therefore, $[ML]_{eq} = 2.46 \times 10^{-5} \text{ mole.l}^{-1}$

$\square (K_f)_{288} = 1.76 \times 10^5 \text{ l.mole}^{-1}$

Calculation of ΔG^0 :

Taking, $\Delta G^0 = -2.303RT \log K_f$ and putting $K_f = 1.76 \times 10^5$ and $T = 288\text{K}$

$\Delta G^0 = -28.92 \text{ KJ.mole}^{-1}$

Experimentation at temperature 301K

From the graph at FIGURE.2: At the point of break in the slope of the curve

$(V_L)^0 = 5\text{ml}$, $(V_M)^0 = 5.6\text{ml}$, and $A_{eq} = 0.681$

$$\frac{(V_M)^0}{(V_L)^0} = \frac{x_M}{x_L} = \frac{5.6}{5} = 1.12$$

Metal : Ligand = 1 : 1

Thus, the above plot predicts one ligand per metal as the composition of the metal complex.

There-fore, formula of the metal complex is ML .

Putting values $[M]_1^0 = [L]_1^0 = 3.3 \times 10^{-5} \text{ mole.l}^{-1}$,

$[M]_2^0 = [L]_2^0 = 1.0 \times 10^{-5} \text{ mole.l}^{-1}$,

$A_1 = 0.729$, $A_2 = 0.277$

in equation (iii)

$$\left(\frac{[M]_1^0 [L]_1^0}{A_1} - \frac{[M]_2^0 [L]_2^0}{A_2} \right) \epsilon_{ML}^2 + ([M]_2^0 + [L]_2^0 - [M]_1^0 - [L]_1^0) \epsilon_{ML} + (A_1 - A_2) = 0$$

we get, $\epsilon_{ML} = 2.39 \times 10^4$ or 1.66×10^4

Putting $\epsilon_M = 3.2 \times 10^2$, $\epsilon_L = 2.665 \times 10^4$, $A_{eq} = 0.681$, $[M]^0 = 3.73 \times 10^{-5} \text{ mole.l}^{-1}$, $[L]^0 = 3.33 \times 10^{-5} \text{ mole.l}^{-1}$ and taking each value of ϵ_{ML} in equation (ii), $[ML]_{eq}$ has been calculated.

Taking $\epsilon_{ML} = 2.39 \times 10^4$ we get $[ML]_{eq} = 7.09 \times 10^{-5} \text{ mole.l}^{-1}$ which is not acceptable.

Taking $\epsilon_{ML} = 1.66 \times 10^4$ we get $[ML]_{eq} = 2.10 \times 10^{-5} \text{ mole.l}^{-1}$ which is acceptable.

Therefore, $[ML]_{eq} = 2.10 \times 10^{-5} \text{ mole.l}^{-1}$



$$(K_f)_{301} = 1.05 \times 10^5 \text{ l.mole}^{-1}$$

Calculation of ΔG^0 :

Taking, $\Delta G^0 = -2.303RT \log K_f$ and putting $K_f = 1.05 \times 10^5$ and $T = 301\text{K}$

$$\Delta G^0 = -28.94 \text{ KJ.mole}^{-1}$$

Calculation of ΔH^0 :

At $T = 288\text{K}$, $(K_f)_{288} = 1.76 \times 10^5 \text{ l.mole}^{-1}$

At $T = 301\text{K}$, $(K_f)_{301} = 1.05 \times 10^5 \text{ l.mole}^{-1}$

$$\text{Taking equation, } \log \left(\frac{K_f^{301}}{K_f^{288}} \right) = \frac{\Delta H^0}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

We get, on calculation, $\Delta H^0 = -28.69 \text{ KJ.mole}^{-1}$

Calculation of ΔS^0 :

At temperature 301K, taking $\Delta G^0 = -28.94 \text{ KJ.mole}^{-1}$,

$$\Delta H^0 = -28.69 \text{ KJ.mole}^{-1} \text{ we get}$$

$$\Delta S^0 = +8.30 \times 10^{-4} \text{ KJ.K}^{-1}.\text{mole}^{-1}$$

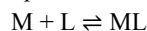
V. DISCUSSION

In present study a regular V-shape graph has been obtained. C. Y. Huang in his research paper titled “Determination of Binding Stoichiometry by the Continuous Variation Method: The Job Plot Methods in Enzymology” has reported that the maximum or minimum on Job’s plot corresponds to the stoichiometry of the two binding species [19]. The reason behind appearance of regular V-shape instead inverted V lies in values of molar attenuation coefficient (ϵ) of species M, L, ML. The order at working wavelength is:

$$\epsilon_M < \epsilon_{ML} < \epsilon_L$$

VI. CONCLUSION

There is 1:1 ligand to metal interaction during complexation process between [CuEohacp] and RbAp forming hetero-binuclear complex [CuEohacpRbAp], and it may be represented as:



This supports the structure proposed for the hetero-binuclear complex [CuEohacpRbAp] during characterization by other analytical techniques.

Characteristic V-shape graph obtained in plot Absorbance Vs. Volume of variant excludes possibility of formation of a 2:2 complex or such higher compositions.

$$(K_f)_{288} = 1.76 \times 10^5 \text{ l.mole}^{-1},$$

$$(K_f)_{301} = 1.05 \times 10^5 \text{ l.mole}^{-1}$$

$$(\Delta G^0)_{288} = -28.92 \text{ KJ.mole}^{-1},$$

$$(\Delta G^0)_{301} = -28.94 \text{ KJ.mole}^{-1}$$

$$\Delta H^0 = -28.69 \text{ KJ.mole}^{-1}$$

$$\Delta S^0 = +8.30 \times 10^{-4} \text{ KJ.K}^{-1}.\text{mole}^{-1}$$

The perusal of result reveals that complexation process is spontaneous at ordinary temperatures, exothermic, and entropically favourable. Further, complexation is more favourable at lower temperatures. The high values of formation constant indicate that hetero-binuclear complex [CuEohacpRbAp] is highly stable at ordinary temperatures, and copper (II) complex of Schiff base [CuEohacp] is a good chelating agent.



VII. CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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