# Spectrophotometric study of stability constants of Semicarbazone-Cu(II) complex at different temperatures

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**ABSTRACT**

*The formation of cupper(II) complex with semicarbazone has been studied spectrophotometrically at an absorption maximum of 700 nm at different temperatures. The data shows that copper(II) and famotidine combine in the molar ratio of 1: 1 . The stability constants of the complex were calculated to be $9.33 \times 10^4$ , $8.51 \times 10^4$ , and $7.41 \times 10^4$ by continuous variation method and $3.28 \times 10^5$ , $3.05 \times 10^5$, and $2.53 \times 10^5$ by mole ratio method at $30^o$, $40^o$, and $50^o$ C, respectively.*
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## INTRODUCTION

Copper(II) edifices assume a vital part in the dynamic locales of a substantial number of metalloproteins in natural frameworks and potential application for various synergist forms in living beings that include electron exchange responses or enactment of some antitumor substances [1]. These procedures are additionally included inbioinorganic [2] and therapeutic science [3]. Truth be told copper(II) chelates have been found to interface with organic frameworks and to display antineoplastic action [4–6] and antibacterial, antifungal [7, 8], and anticancer movement [9]. Some copper(II) N,S,O/N,N-contributor chelators are great anticancer operators because of solid restricting capacity with DNA base pair [10]. Synthesis of oximes and semicarbazone and their complexes with different transition metals are accounted for in the writing and observed to be dynamic as antibacterial , subterranean insect tubercular ,antilepral, antiviral , hostile to malarial tumors pesticide herbicide anticonvulsant action and sleep inducing properties or the capacity of some of their Cu(II) buildings to copy superoxide dismutase action Semicarbazone edifices of some metal particles have been accounted for .In this paper, a novel arrangement of move metal edifices with oxime and semicarbazone were incorporated and they were screened for antimicrobial exercises. The vast majority of the buildings were indicated moderate to great antibacterial and antifungal movement [11].

## MATERIALS AND MEHTODS

**Apparatus**
Spectrophotometric measurements were performed on a UV-1700Shimadzu double beam spectrophotometer (Japan) using matched 10mm quartz cells. A Horiba F.8pH meter.

**Reagents**
All the compounds and solvents used were purchased from Aldrich and Sigma and used as received without further purification.

## RESULTS AND DISCUSSION

**The Method of Continuous Variation (Job's Method)**
Cu(II) nitrate standard solution $1*10^{-4}$ M was pippetted into volumetric flasks (0, 1, 2,,….6ml) and a solution of $1*10^{-4}$ M semicarbazone (6, 5, 4,…0ml) was added. Respectively keeping the mole ratio constant. all the measurements were made at 700nm at three temperatures (30, 40, and $50^0$C) as shown in (Table 1).
The results shows that continuous variation method shows a maximum at the mole fraction of 0.5 for Cu(II)-Semicarbazone complex, indicating the formation of 1:1 complex is formed as shown in (Fig .1).

The corresponding equation used in this study for Job's method is as follows[12,13]:
$$K_f = [ML_2] / [M][L]^2 \quad \text{for 1:2}$$

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$$K_f = [ML] / [M][L] \qquad \text{for 1:1}$$

The corresponding thermodynamic parameters (ΔG,ΔH, and ΔS) were derived and discussed.
The enthalpy ( ΔH) for the complexation process was calculated from the slope of the plot log K vs. 1/T as shown in (Fig. 2) using the graphical representation of van't Hoff equations as following:

$$\Delta G = -2.303 \, RT \log K = \Delta H - T \Delta S$$
Or
$$\text{Log} K = [-\Delta H/2.303R][1/T]+[\Delta S/2.303R]$$

where R gas constant = 8.314 J.mol . K , K is the formation constant for the complex and T is the temperature (K).
From the ΔG and ΔH values, one can deduce the entropy ΔS using the well known relationship : ΔS = (ΔH-ΔG)/T

The following remarks can be pointed out:
(1)  The negative value of ΔH mean that the composition process are exothermic.
(2)  The stability constants ( logK) for complexe decrease with increasing temperature.
(3)   The negative values of ΔG for the complexe formation suggest a spontaneous nature of such process.
(4)  The positive values of ΔS confirming that the complex formation processes is entropically favorable[14].

**The molar ratio method**
In the molar ratio method , the concentration of the metal ion was kept constant at $0.72*10^{-3}$M while the ligand of semicarbazone was varied as shown in (Table 3). The absorbance of sample solution was measured against blank at the maximum wavelength[15]. The absorbance values were then plotted against the ratio of [L]/[M] as shown in (Fig .3). The inflection of the line obtained shows the molar ratio of 1:1 complex is formed.

Result obtained from molar ratio and continuous variation methods are in agreement with each others. The corresponding thermodynamic parameters (ΔG,ΔH, and ΔS) were derived and discussed[16,17].

**Table 1. Experimental data of Cu(II)-Semicarbazone by continuous variation method**

| NO | Metal conc ($*10^{-4}$moles) | Ligand conc ($*10^{-4}$moles) | $X_{Cu}$ | Absorbance at 700nm | | |
|----|----|----|----|----|----|----|
| | | | | $30^0$C | $40^0$C | $50^0$C |
| 1 | 0 | 1.44 | 0 | 0.0445 | 0.0613 | 0.0585 |
| 2 | 0.24 | 1.2 | 0.17 | 0.1018 | 0.1107 | 0.1079 |
| 3 | 0.48 | 0.96 | 0.33 | 0.1666 | 0.1659 | 0.16 |
| 4 | 0.72 | 0.72 | 0.5 | 0.2195 | 0.2315 | 0.2031 |
| 5 | 0.96 | 0.48 | 0.66 | 0.1988 | 0.2093 | 0.1868 |
| 6 | 1.2 | 0.24 | 0.83 | 0.074 | 0.0957 | 0.0762 |
| 7 | 1.44 | 0 | 1 | 0.0063 | 0.0042 | 0.0013 |

**Table 2. All the thermodynamic parameters of Cu(II)-Semicarbazone complex by continuous variation method**

| Compound | Temperature(K) | Formation constant ($K_f$) | $\log K_f$ | Gibbs energy KJmol$^{-1}$ (ΔG) | Enthalpy change KJmol$^{-1}$ (ΔH) | Entropy change KJmol$^{-1}$ (ΔS) |
|----|----|----|----|----|----|----|
| Cu(II)-Semicarbazone complex | 303 | $9.33X10^4$ | 4.97 | $-2.88X10^4$ | $-1.12X10^3$ | 9.15X101 |
| | 313 | $8.51X10^4$ | 4.93 | $-2.95X10^4$ | | 9.08X101 |
| | 323 | $7.41X10^4$ | 4.87 | $-3.01X10^4$ | | 8.98X101 |

**Table 3. Experimental data of Cu(II)-Semicarbazone by molar ratio method.**

| NO | Metal conc ($*10^{-4}$moles) | Ligand conc ($*10^{-4}$moles) | [L]/[M] | Absorbance at 700nm | | |
|----|----|----|----|----|----|----|
| | | | | $30^0$C | $40^0$C | $50^0$C |
| 1 | 0.72 | 2.52 | 3.5 | 0.2335 | 0.2435 | 0.2122 |
| 2 | 0.72 | 2.16 | 3 | 0.2275 | 0.2546 | 0.1989 |
| 3 | 0.72 | 1.8 | 2.5 | 0.2367 | 0.2473 | 0.2168 |
| 4 | 0.72 | 1.44 | 2 | 0.2229 | 0.2445 | 0.1961 |
| 5 | 0.72 | 1.08 | 1.5 | 0.2593 | 0.2607 | 0.248 |
| 6 | 0.72 | 0.72 | 1 | 0.1939 | 0.2167 | 0.1623 |
| 7 | 0.72 | 0.36 | .05 | 0.1524 | 0.1557 | 0.1569 |
| 8 | 0.72 | 0 | 0 | 0.0016 | 0.0007 | 0.0043 |

**Table 4. Thermodynamic parameters of Cu(II)-Semicarbazone complex by molar ratio method**

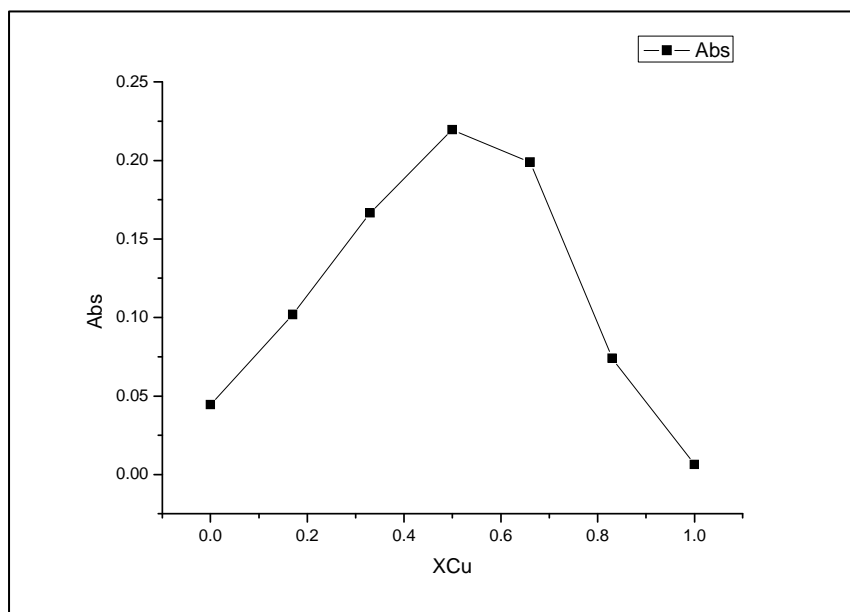| Compound | Temperature(K) | Formation constant ($K_f$) | $\log K_f$ | Gibbs energy KJmol$^{-1}$ (ΔG) | Enthalpy change KJmol$^{-1}$ (ΔH) | Entropy change KJmol$^{-1}$ (ΔS) |
|----|----|----|----|----|----|----|
| **Cu(II)-Semicarbazone complex** | 303 | $3.28X10^5$ | 5.52 | $-3.20X10^4$ | | $1.01X10^2$ |
| | 313 | $3.05X10^5$ | 5.48 | $-3.29X10^4$ | | $1.01X10^2$ |
| | 323 | $2.53X10^5$ | 5.40 | $-3.34X10^4$ | $-1.27X10^3$ | $9.95X10^1$ |

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**Fig1. Cu(II)-Semicarbazone complex stoichiometry determination by spectrophotometric measurements at 700nm**
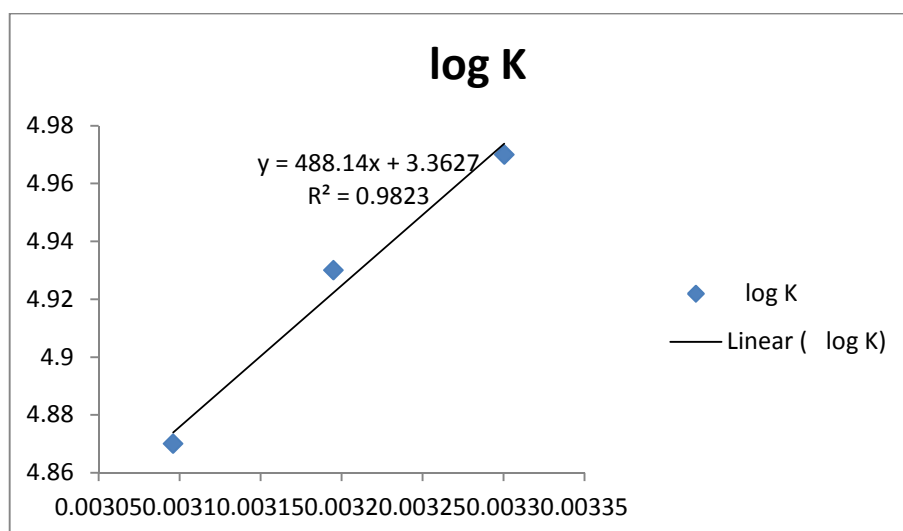


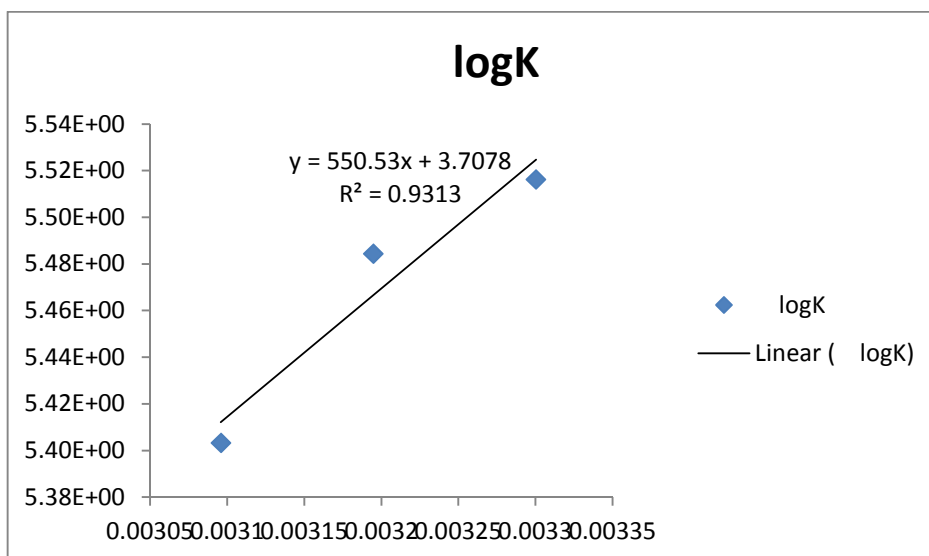**Fig 2. logK against 1/T for the Cu(II)-Semicarbazone complex**



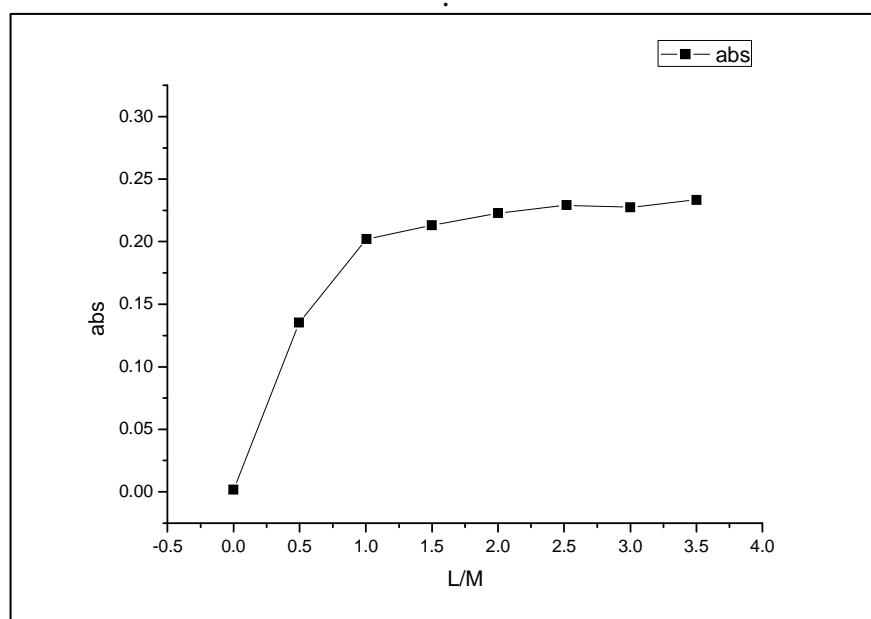**Fig 3. Curve for molar ratio method of Cu(II)-Semicarbazone complex**

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**Fig 4 logK against 1/T for the Cu(II)-Semicarbazone complex by molar ratio**

The enthalpy ( $\Delta H$) for the complexation process was calculated from the slope of the plot log K vs. 1/T as shown in (Fig.4) and all the thermodynamic parameters of divalent-Semicarbazone complex by molar ratio method are recorded in (Table 4).

The following remarks can be pointed out [18]:
(1) The negative value of $\Delta H$ mean that the composition process are exothermic.
(2) The stability constants ( logK) for complexes decrease with increasing temperature.
(3) The negative values of $\Delta G$ for the complexes formation suggest a spontaneous nature of such process.
(4) The positive values of $\Delta S$ confirming that the complex formation processes is entropically favorable.

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