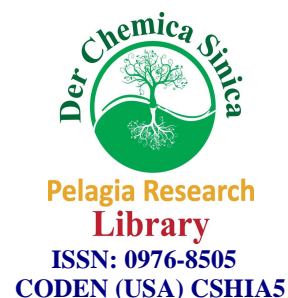




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Spectrophotometric Studies on stability constant of chlorosubstituted pyrazoles with Cu (II) Nd (III) and Tb (III) metal ions at 0.1 M Ionic strength

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ABSTRACT

The stability constant of complexes of Cu (II) metal ion with 3-(4-Chlorophenyl)-4-(2-chlorophenyl benzoyl)-5-(2-hydroxy phenyl)-pyrazole -L₃ and 3-(4-Chlorophenyl)-4-(2-furanoyl)-5-(2-hydroxy phenyl)-pyrazole -L₄ by Isobestic point method at wavelength 525 nm and 500 nm respectively and Cu (II), Nd (III) and Tb (III) metal ions with 3-(2-Hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4-methoxy phenyl)-1-phenyl pyrazole -L₁, 3-(2-Hydroxy-3,5-dichlorophenyl)-4-anisoyl-5-(4-methoxy phenyl)-1-phenyl -Δ²-pyrazoline -L₂ and 3-(4-Chlorophenyl)-4-(2-chlorophenyl benzoyl)-5-(2-hydroxy phenyl)-pyrazole -L₃ were determined by Job's method. The measurement of absorbance was done by spectrophotometer. The conditional stability constants (log K) were calculated from the equilibrium constant (K) which obtained from the measured absorbance. The log K values were used to study the confirmation of complex formation.

Keyword: Stability constant, Chlorosubstituted pyrazoles, Isobestic point and Job's method, spectrophotometer.

INTRODUCTION

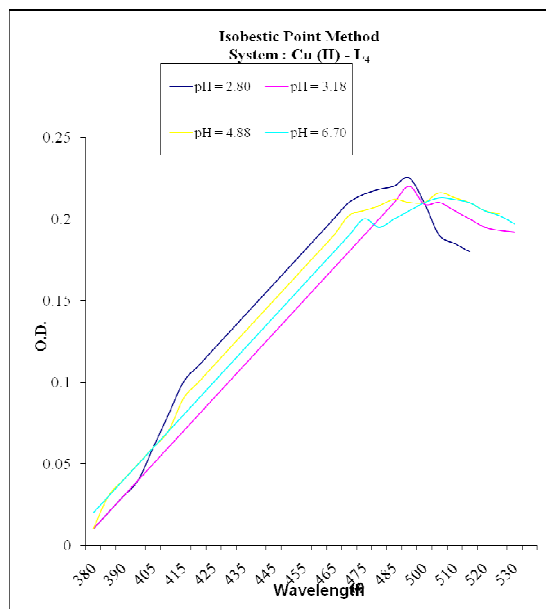
The spectrophotometric is one of the important branch of science which has played an important tool for determining the structure of organic and inorganic compounds. Spectroscopy deals with the study of measurement of interaction between radiation energy and matter particles and it can also be used to measure the stability constants. The stability constants of metal complexes have been determined by different methods such as spectrophotometric and potentiometry. Spectrophotometric methods are more suitable for studying chemical equilibrium in solution and it has been used for equilibrium constant for many decades [1, 2]. Spectrophotometric methods are not limited to any pH range and it is one of the most powerful methods for investigation of the solution equilibrium. Spectrophotometric study of 4-(4-chlorophenylazo)-3-methyl-1-[2-hydroxy-3-morpholinopropane-1-yl]-2-pyrazoline-5-one and its metal complexes has been done by El-Bindary [3]. The complex formation is confirmed by using Isobestic point method and Job's variation method at a fixed temperature studied by Agrawal [4] for metal complex of Co (II) with substituted thiazolones. Naik *et al* [5] have studied the stability constants of substituted pyrazoles and pyrazolines with rare earth metal ions by spectrophotometrically. The conditional stability constants and confirmation of complex formation of Cu (II), Ni (II) and Co (II) complexes with captopril using spectrophotometric technique was reported by Narwade [6]. The conditional stability constant of the complexes

were determine from Yoe and Jones mole ratio method [7] and Job's continuous variation method. The Job's method of continuous variation used for the determination of metal ligand stability constant [8] and confirmation of complexes has been studied by McBoyde [9]. The Vosburgh and Coworker [10] modified the Job's method. Khobragade [11] has investigated Co (II) - peptide complex formation spectrophotometrically by Isobestic point and Job's method. Raghuwanshi *et al* [12] have studied the confirmation of complex formation by Isobestic and Job's method between Cu (II) and substituted isoxazolines spectrophotometrically. Aktas *et al* [13] have determined pKa values of phenolic compounds in acetonitrile-water mixture using spectrophotometric measurements at various pH values. In the present investigation, the metal – ligand stability constants and confirmation of complexes of some chlorosubstituted pyrazoles and pyrazolines with Cu (II), Nd (III) and Tb (III) metal ions were determined at 0.1 M ionic strength by addition of appropriate of sodium hydroxides. Absorption was measured by using uv-visible spectrophotometer of model 1700 Shimadzu. The chlorosubstituted pyrazoles, pyrazolines and their complexes have wide applications in the various field such as medicinal [14], agricultural industries [15] and pharmaceuticals [16].

MATERIALS AND METHODS

Chlorosubstituted pyrazoles and pyrazoline are antibiotic drugs having many applications for living organism. It has been synthesized in laboratory by standard method [17, 18]. All chemicals were used of AR grade. Dioxane was purified by described method [19]. UV-Visible spectrophotometer model 1700 Shimadzu was used in the present work. In the present study, the equimolar (0.01 M) solutions of metals such as Cu (II), Nd (III), and Tb (III) were prepared in distilled water and ligands (L₁, L₂, L₃, and L₄) in dioxane. These solutions were mixed in different proportions to keep the total volume of each solution constant to 5 ml as described by Job's. The measurements for optical density were made at after adjusting the appropriate pH (2 to 3) and appropriate wavelength at 0.1M ionic strength and 27± 0.1°C. The pH of each solution was maintained by using the buffer solution. Then each solution was diluted by adding 2 ml of solvent (dioxane) and again optical densities were measured. Vereille's Isobestic point method was used to study the complex formation, for the systems as Cu (II)-L₃ and Cu (II)-L₄ at different pH. The similar observations noted for all systems.

Figure 1. Plots of wavelength (nm) Vs optical density (O.D.) for System: Cu (II)-L₄

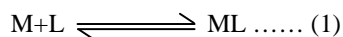


RESULTS AND DISCUSSION

When the ligand solution are mixed with the metal ions solution then it was observed that the color of solutions was light yellow bellow 2.6 pH and light pink above 6.5 pH for Cu (II)-L₃ and Cu (II)-L₄ systems. This indicates the complex formation between metal ion and ligand species. To prevent the oxidation of the ligand at higher pH during spectrophotometric measurements, the optical density measured immediately after the preparation of the solution.

The absorption data obtained are used to plot the curves. The curves plotted between wavelength (nm) and optical density (O.D.). From figure 1, the numbers of absorption curves are intersecting at a point (Isobestic point) at 525 nm and 500 nm respectively. This indicates the formation of 1:1 and 1:2 complexes.

The conditional stability constants of complexes are determined spectrophotometrically. Spectrophotometric analysis is based on the variation of color intensity of the systems with changing concentration of the component. It is concerned with determination of the concentration of the substances present in solution and metal-ligand stability constant of the complex. The graph plotted of the optical density against percent composition of the metal. The metal-ligand stability constant can be obtained by equation (2).



$$K = \frac{[ML]}{[M][L]} \dots\dots\dots (2)$$

The concentration of complex 'x', [ML] in any metal-ligand solution was obtained by Job's curve, if the initial concentrations of metal [M] and ligand [L] in a particular solution are 'a' and 'b' then the equilibrium constant 'K' can be determined by the help of simple law of mass action.

$$K = \frac{x}{(a - x)(b - x)} \dots\dots\dots (3)$$

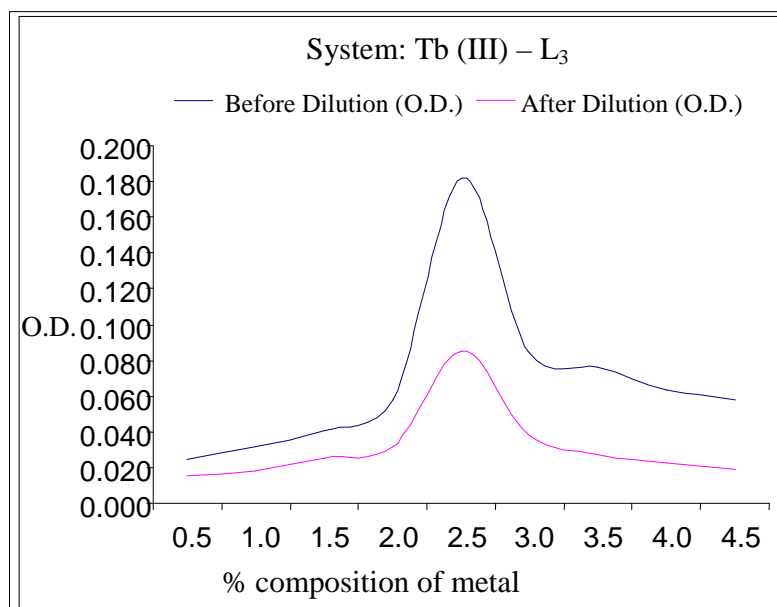
K = Conditional stability constant of complex, x = Concentration of complex, a = Concentration of metal ions, b = Concentration of ligand.

**Table 1. System: Tb (III) → L₃ in dioxane.
λ_{max} = 675 nm p^H = 2 – 3**

Metal ion (ml)	Ligand (ml)	Optical Density (O.D.)	
		Before dilution	After dilution
0.5	4.5	0.024	0.015
1.0	4.0	0.032	0.018
1.5	3.5	0.041	0.025
2.0	3.0	0.058	0.032
2.5	2.5	0.182	0.085
3.0	2.0	0.084	0.038
3.5	1.5	0.076	0.027
4.0	1.0	0.063	0.023
4.5	0.5	0.058	0.019

Table 2. Log K values of conditional stability constant by spectrophotometric technique

Complex	λ _{max}	Spectrophotometric log K
Cu (II) – L ₁	700 nm	4.4818
Nd (III) – L ₁	680 nm	6.3413
Cu (II) – L ₂	685 nm	3.9893
Nd (III) – L ₂	460 nm	5.3115
Cu (II) – L ₃	680 nm	3.3089
Tb (III) – L ₃	675 nm	3.5379

Figure 2. System: Tb (III) \rightarrow L₃ in dioxane.

The log K gives the conditional stability constant. The representative example is one of the systems shown in Table 1 and Figure 2. The curves were constructed between the values of optical density and percentage composition of metal ions. The conditional stability constant (log K) were calculated from the curves and the values of log K are reported in the Table 2.

It is observed from the Table 2, the conditional stability constants values are found to be greater for lanthanide metals complex as Nd (III) – L₁, Nd (III) – L₂, Tb (III) – L₃ than transition metal complex Cu (II) – L₁, L₂, and L₃ may be due to the higher oxidation state of Nd (III) and Tb (III) than Cu (II), hence effective nuclear charge of Nd (III) and Tb (III) is more than Cu (II). As a results lone pair acceptance capacity of Nd (III) and Tb (III) ions increases during the formation of complex and so the values of log K for Nd (III) and Tb (III) ions are greater. The conditional stability constants are found to be lesser than the real stability constants [obtained from p^H – metric measurements [20] except Cu (II) – L₂] and are represented in Table 3. The agreement between the values obtained by both the techniques is fairly good. This may due to the fact of attribution to the simultaneous complex formation.

Table 3. Comparison of log K values between p^H – metric and spectrophotometric Technique.

Complex	p ^H metric (log K)	Spectrophotometric (log K)
Cu (II) – L ₁	5.9440	4.4813
Nd (III) – L ₁	7.5440	6.3413
Cu (II) – L ₂	3.4313	3.9893
Nd (III) – L ₂	6.1430	5.3115

CONCLUSION

On the basis of the above discussion it may be concluded that the figure 1 showed that the formation of 1:1 and 1:2 complexes because the numbers of absorption curves are intersecting at a point (Isobestic point) at 525 nm and 500 nm respectively. It is also observed that from the above results are clearly indicates that the interaction of ligands with metal ions will directly affect the complex formation and due to that changes occur in log K values. The change occur in log K values due to the factors such as effective nuclear charge, oxidation number, size of metal ion are also affect complex formation. The log K values in the Table 2 and 3 clearly indicate the complexes are formed.

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