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Complex Formation of Co(II) and Cu(II) Metal Ion Complexes with Substituted Isoxazolines

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The interactions of Co(II) and Cu(II) with 3-(2′-hydroxy-4′-methyl-5′-chlorophenyl)-4-(2′-chlorobenzoyl-5-(4′-N,N-dimethyl aminophenyl) isoxazoline (Ligand I), 3-(2′-hydroxy-4′-methyl-5′-chlorophenyl)-4-(2′-chlorobenzoyl)-5-(4′-methoxy phenyl) isoxazoline (ligand II) and 3-(2′-hydroxy-4′-methyl-5′-chlorophenyl)-4-(2′-chlorobenzoyl)-5-phenyl isoxazoline (ligand III) have been studied by spectrophotometric technique at 0.1 M ionic strength and (30 ± 0.1°C) in 70% dioxane-water mixture. The data obtained were used to estimate the values of metal-ligand stability constant of substituted isoxazoline. Spectrophotometric investigation of Co(II) and Cu(II) complexes with ligand (I), ligand (II) and ligand (III) showed 1 : 1 complex formation. The formation of complexes has been studied by Job's variation method. The results obtained of stability constants are in good agreement.

Key Words: Stability constants, Complex formation, Co(II), Cu(II), Isoxazoline.

INTRODUCTION

Substituted isoxazolines are good complexing agents due to the presence of electron donor oxygen. They form coloured complexes with metal ions. Rowland and Meloan[1] investigated cinnamohydroxomic acid chelates spectrophotometrically and reported the composition and the molar extinction coefficients of these chelates. Khobragade *et al.*[2] have investigated the metal-ligand stability constants of UO_2(II) and Cu(II) complexes with some substituted sulphonic acids. Narwade *et al.*[3] have studied Fe(III) complexes with some substituted chalcones spectrophotometrically. Narwade *et al.*[4] have investigated the stability constants of some lanthanide ions with sulphonic acid spectrophotometrically. The metal chelates of hydrazo-dimedone dynes are studied by Atef *et al.*[5] Sunita and Gupta[6] have worked on spectrophotometric determination of cyanide in biological complex using a new reagent. Manimekalai *et al.*[7] have determined the stability constants and composition of 3-(2-furanyl)-2-propenhydroxomic acid chelates by Job's method at continuous variations in 30% ethanol-water medium. Chavan and

Joshi[8] have studied the spectrophotometric determination of micro amounts of gold(III) using cyclopentane-spiro 2′-(1′-methyl-2′,4′-dithio)-5-triazine. Sawalakhe[9] also determined stability constant and composition of the Fe(III)-1-(2-hydroxy phenyl-3-phenyl-1,3-propandione) chelates by Job's method in 70% dioxane-water mixture. Bhargava and Tondon[10] determined the metal-ligand stability constant of Pt(IV) with substituted alkyl/aryl thiourea complexes spectrophotometrically. Sawalakhe *et al.*[11] studied the interaction of metals with 1,3-diketone, pyrazole and pyrazolines spectrophotometrically. Mandakmare *et al.*[12] studied the stability constant of $UO_2(II)$ complexes with some substituted coumarins at 0.1 M ionic strength spectrophotometrically. Zabeen *et al.*[13] investigated 1 : 1 complex formation of 3-hydroxy-3-methyl-1-O-carboxy phenyl triazene with palladium by using spectrophotometric technique. Raghuwanshi *et al.*[14] studied the conditional stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Conditional stability constants of transition metal ions with some amino acid peptides have been studied by Sondawale and Narwade[15]. Meshram *et al.*[16–18] investigated the metal-ligand stability constants of transition metal ion complexes with some substituted isoxazolines by spectrophotometric and pH-metric techniques. Acoustical properties of peptides were studied in 20% methanol-water mixture by Sondawale *et al.*[19]. Agrawal *et al.*[20] determined the metal-ligand stability constants of some substituted thiadiazoles spectrophotometrically. Raut *et al.*[21] studied the conditional stability constants of transition metal ion complexes with the antibiotic drug captopril.

After review of literature survey, it was thought of interest to study the chelating properties of some newly subsitituted isoxazolines with Co(II) and Cu(II) metal ions by Job's variation method under suitable conditions spectrophotometrically.

EXPERIMENTAL

All the chelating agents have been synthesized in the laboratory and the compounds were crystallized before use. Substituted isoxazolines are insoluble in water and hence 70% dioxane-water (v/v) was used as solvent.

The metal-ligand stability constants of some newly substituted isoxazolines were determined spectrophotometrically. The nitrates of cobalt and copper were used and their solutions were prepared in double distilled water. The solution of potassium nitrate was prepared (0.1 M) and used for maintaining ionic strength constant.

Systronics spectrophotometer No. 108 was used for measuring absorption of solution.

The following systems were chosen for spectrophotometric measurements:

(1) Co(II)-Ligand (I); (2) Cu(II)-Ligand (I);
(3) Co(II)-Ligand (II); (4) Cu(II)-Ligand (II);
(5) Co(II)-Ligand (III); (6) Cu(II)-Ligand (III).

RESULTS AND DISCUSSION

Metal-ligand stability constants and confirmation of complexes have been studied by McBryde[22] and Banerjee[23]. The compositions of the complexes are confirmed by Job's method as modified by Vasburgh and Gold.[24]

The compositions of metal ion solution (1×10^{-2} M) and ligand (1×10^{-2} M) were prepared in ten series. λ_{max} was determined using one of the compositions at which there is maximum absorption. The absorptions for all the compositions were recorded at constant wavelength (λ_{max}). Each solution is diluted up to 15 mL and absorptions are recorded at same λ_{max}. The data of absorption and percentage composition of metal ion and ligand solutions at constant pH can be used and the curves are constructed as shown in Figs. 1–6.

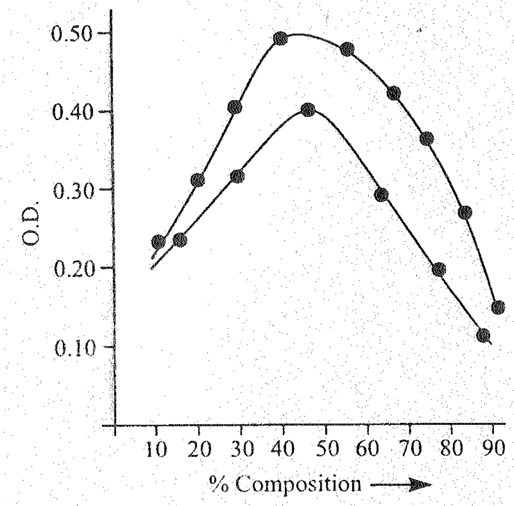

Fig. 1. Plot between per cent composition *vs.* absorption (O.D.) system Co(II)-ligand (I).

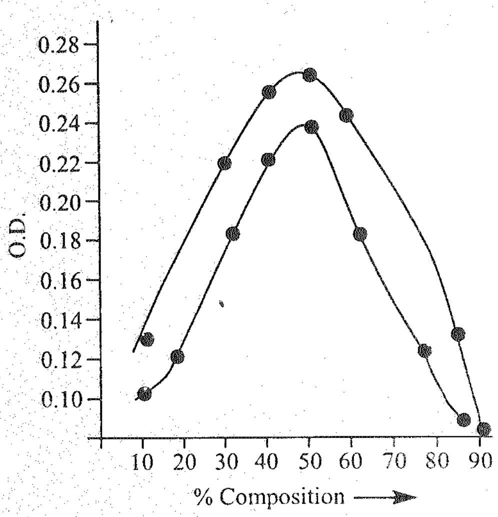

Fig. 2. Plot between per cent composition *vs.* absorption (O.D.) system Cu(II)-ligand (I).

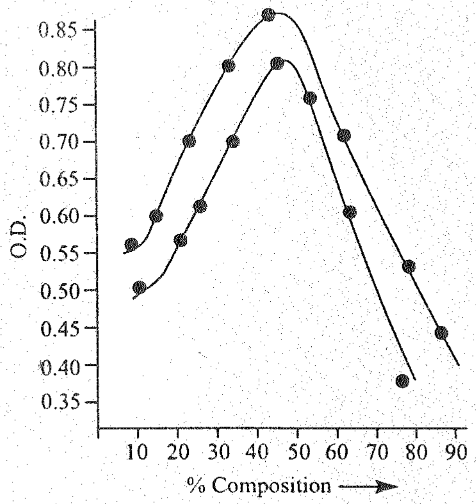

Fig. 3. Plot between per cent composition *vs.* absorption (O.D.) system Co(II)-ligand (II)

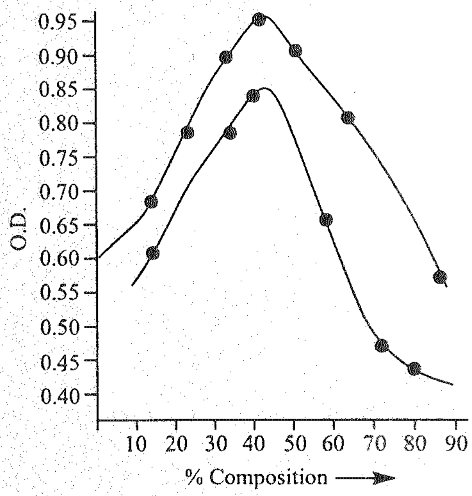

Fig. 4. Plot between per cent composition *vs.* absorption (O.D.) system Cu(II)-ligand (II)

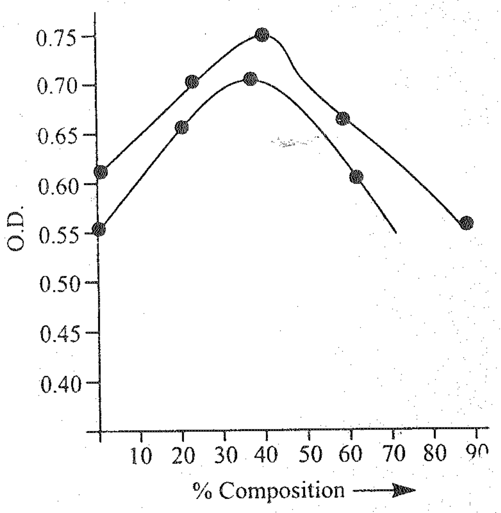

Fig. 5. Plot between per cent composition *vs.* absorption (O.D.) system Co(II)-ligand (III).

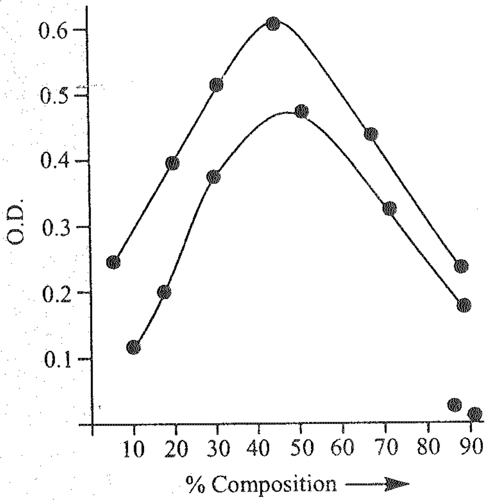

Fig. 2. Plot between per cent composition *vs.* absorption (O.D.) system Cu(II)-ligand (III).

The conditional stability constants of metal-ligand complexes were calculated for all the systems using the following expression:

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \qquad (1)$$

where K = conditional stability constant of complex; x= concentration of complex; a_1 and a_2 = concetrations of metal ions; b_1 and b_2 = concetrations of ligands.

The conditional stability constants obtained by spectrophotometric technique are presented in Table-1.

TABLE-1
CONDITIONAL STABILITY CONSTANT OF SUBSTITUTED ISOXAZOLINES

System	K	log K	log K^1 (Mean)
Co(II)-Ligand (I)	0.6879×10^3	2.9914	3.1754
Cu(II)-Ligand (I)	1.1883×10^3	3.7490	
Co(II)-Ligand (II)	0.9804×10^3	2.8376	
Cu(II)-Ligand (II)	2.1070×10^3	3.3236	
Co(II)-Ligand (III)	0.6784×10^3	2.8315	
Cu(II)-Ligand (III)	2.0846×10^3	3.3194	

It could be seen from Table-1 that the values of conditional stability constants of Cu(II) complexes are greater than the corresponding Co(II) complexes. The greater value of stability constant of Cu(II) complexes may be due to the fact of more stable nature of Cu(II).

The value of stability constant of Cu(II)-Ligand (I) complex is greater than the values of stability constants of Cu(II)-Ligand (II) and Cu(II)-Ligand (III). This may be due to the effect of the powerful electron releasing group such as $N(CH_3)_2$ group in ligand (I). Similar is the case with Co(II) complexes.

Order of stability constants:

Cu(II)-Ligand (I) > Cu(II)-Ligand (II) > Cu(II)-Ligand (III)

Co(II)-Ligand (I) > Co(II)-Ligand (II) > Co(II)-Ligand (III)

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