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Spectrophotometric Investigation of Conditional Stability Constants and Confirmation of Complex Formation of Cu (II) Complexes with Substituted Chalcones and Isoxazolines

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Spectrophotometic investigation on Cu(II) complexes with substituted chalcones and isoxazolines has shown 1 : 1 and 1 : 2 complex formation. The complex formations are confirmed using isobastic point method and Job's variation method at 0.1 M ionic strengtlı and temperature 27 ± 1°C spectrophotometrically. The present method is compared with potentiometric method. The results obtained of stability constants are in good agreement.

INTRODUCTION

In view of analytical application chalcones and isoxazolines ligands are selected in the present investigation. The metal chelates of hydrazo-dimedone dyes are studied by Atef *et al.*[1] Narwade *et al.*[2] have investigated the stability constants of some lanthanide ions with sulphonic acid spectrophotometrically. Sunita and Gupta[3] have worked on spectrophotometric determination of cyanide in biological amples susing a new reagent. Narwade *et al.*[4] have studied Fe(III) complexes with some substituted chalcone by spectrophotometric technique. Raghuwanshi *et al.*[5] have shown 1 : 1 and 1 : 2 complex formation of Cu(II), Co(II), Ni(II) with some substituted chalcones and isoxazolines potentiometrically. Zabeen *et al.*[6] have investigated 1 : 1 complex formation of 3-hydroxy-3-methyl-1-O-carboxy phenyl triazene with palladium by using spectrophotometric technique. Chavan and Joshi[7] have studied the spectrophotometric determination of microamounts of gold(III) using cyclo-pentane-spiro-2'(1'-methyl-2',4'-dithio)-5-triazine. The study of metal-ligand complexes of chalcones and isoxazolines was not studied so far; therefore, the present work has been undertaken to study systematically the confirmation of complexes of 2'-hydroxy-5'-methyl-3-nitrochalcone (1); 2'-hydroxy-3'-nitro-5-methyl-3-nitrochalcone (2); 3-(2-hydroxy-5-methylphenyl)-5-(3-nitrophenyl) isoxazoline (3); 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(3-nitrophenyl) isoxazoline (4) with copper metal ion using isobastic point method and Job's variation method.

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EXPERIMENTAL

All the chelating agents have been synthesized in the laboratory using Doshi and Ghiya method[8] and the compounds were recrystallized from ethanol before use.

Copper nitrate salt (BDH) and sodium perchlorate (BDH) were used and their solutions were prepared in double distilled water (*i.e.*, Cu(II) = 0.01 M and $NaClO_4$ = 0.1 M). Chelating agent solutions were prepared in 1, 4-dioxane. Visible Spectrophotometer No. 118 was used in the present work for measurement of absorption of the solution.

RESULTS AND DISCUSSION

Spectrophotometric Measurements

(a) ***Isobastic Point Method:*** Vareille's[9] method of isobastic point was used to study the complex formation between Cu(II) and substituted chalcones and isoxazolines. The absorption spectra were measured for solution containing copper metal ion (5×10^{-4} M) and ligand (100×10^{-4} M) at pH value ranging from 2.0 to 7.0. The pH of solution was measured by means of standardised pH-meter. The data of absorption corresponding to wavelength in nm for all the pH solutions were used to construct the curves (a representative curve is shown in Fig 1 with ligand 1). Most of the curves are intersecting at a point (Isobastic point). The curves are intersecting at 515 nm, 535 nm, 528 nm and 540 nm for ligand 1 to 4 respectively. This indicates the presence of two complex species (*i.e.* 1 : 1 and 1 : 2 complexes) in the pH range investigated. Potentiometric tecnique also showed the presence of two complex species of Cu(II) complexes with substituted chalcones and isoxazolines[5].

(b) ***Job's Method:*** Job's variation method was adopted to know the nature of complexes. The solutions of Cu(II) [1×10^{-2} M] and ligands [1×10^{-2} M] were prepared in 70% dioxane-water mixture and ionic strength was maintained constant (0.1 M) by adding an appropriate amount of 1 M sodium perchlorate solution. The pH value of each composition was adjusted constant by adding suitable amount of either HCl solution or NaOH solution. λ_{max} was determined using one of the compositions at which there is maximum absorption.

The absorptions for all the compositions were recorded at a constant wavelength λ_{max}. The data of absorption and % compositions are presented in Tables-1 to 4 and used to construct the curves for all the systems (a representative curve for ligand 1 is shown in Fig. 2).

It was observed that 1 : 1 complex formation occurs at pH 3.0 for Cu (II)complexes with all the ligands. 1 : 1 complex formation was also confirmed at about pH 3.0 by means of potentiometric technique using Irving and Rossotti's method[10].

Conditional stability constants of metal-ligand complexes were calculated for all the systems and presented in Table-5. It can be seen from Table-5 that conditional stability constants of systems 2 and 4 are lower than the values of systems 1 and 3. It may be due to the presence of nitro group in ligand no. 2 and ligand no. 4.

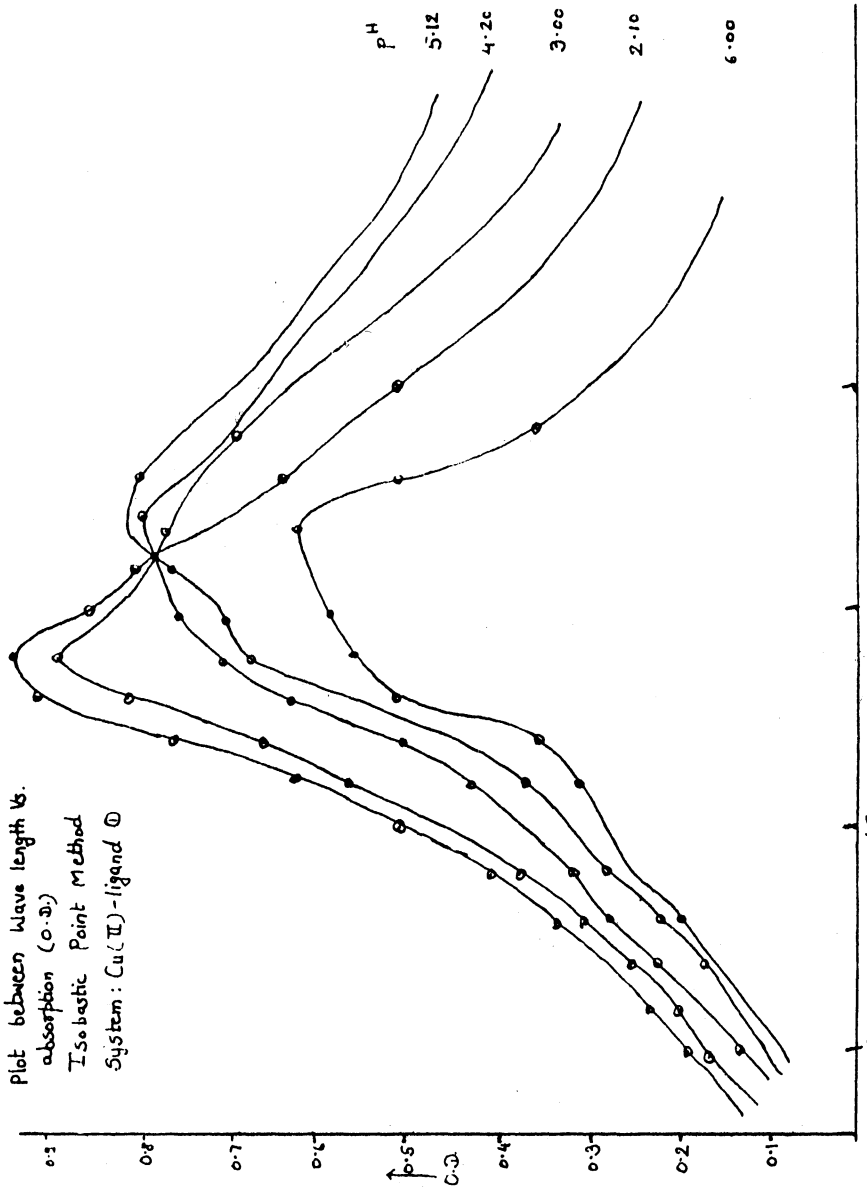
Plot between wave length Vs.
absorption (O.D)
Isobestic Point Method
System : Cu(II)-ligand ①
pH
5·12
4·20
3·00
2·10
6·00
O.D
Wave length λ →
400
450
500
550
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9

Fig. 1

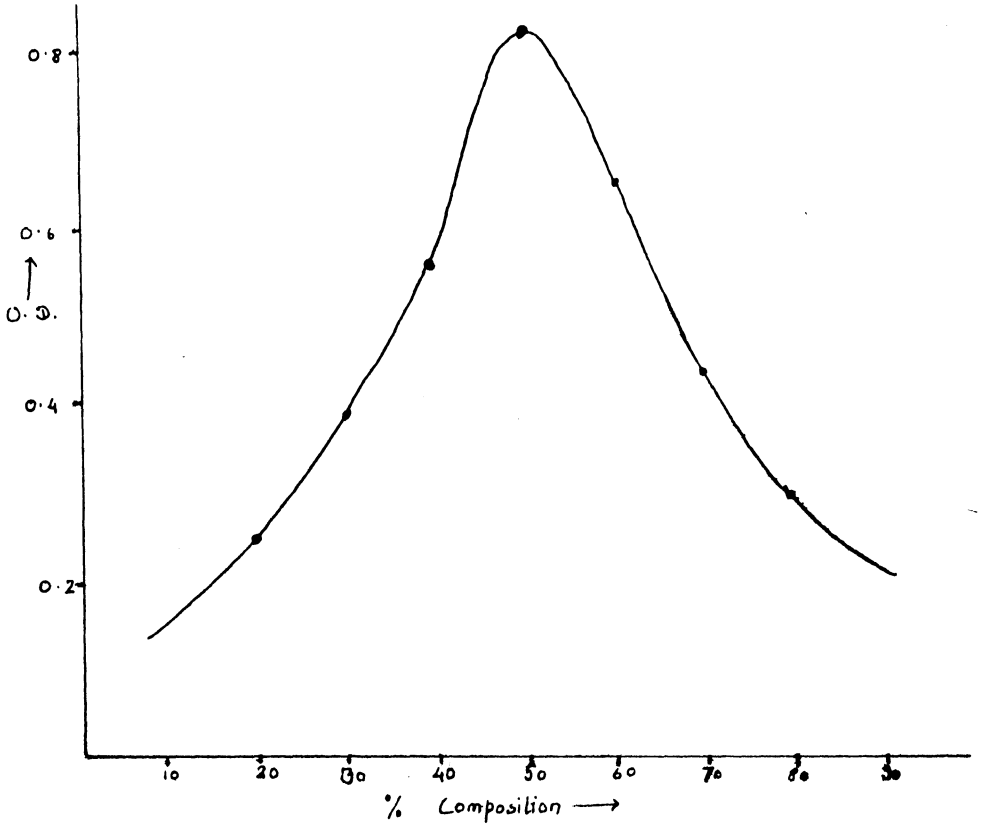

Fig. 2 Plot between % composition *versus* absorption (O.D.) λ_{max} = 480 nm; system Cu(II)—ligand no. 1.

TABLE-1
DATA OF ABSORPTION AND % COMPOSITION FOR LIGAND NO. 1 (λ_{max} = 480 nm).

Metal	Ligand	Absorption (Optical density)
2	18	0.16
4	16	0.25
6	14	0.38
8	12	0.54
10	10	0.81
12	8	0.63
14	6	0.42
16	4	0.29
18	2	0.21

TABLE-2
DATA OF ABSORPTION AND % COMPOSITION
FOR LIGAND NO. 2 (λ_{max} = 510 nm)

Metal	Ligand	Absorption (Optical density)
2	18	0.23
4	16	030
6	14	0.49
8	12	0.67
10	10	0.91
12	8	0.61
14	6	0.52
16	4	0.33
18	2	0.23

TABLE-3
DATA OF ABSORPTION AND % COMPOSITION FOR
LIGAND NO. 3 (λ_{max} = 495 nm)

Metal	Ligand	Absorption (Optical density)
2	18	0.19
4	16	027
6	14	0.39
8	12	0.67
10	10	0.79
12	8	0.83
14	6	0.59
16	4	0.43
18	2	0.27

TABLE-4
DATA OF ABSORPTION AND % COMPOSITION FOR
LIGAND NO. 4 (λ_{max} = 520 nm)

Metal	Ligand	Absorption (Optical density)
2	18	0.26
4	16	0.41
6	14	0.58
8	12	0.65
10	10	0.89
12	8	0.80
14	6	0.64
16	4	0.52
18	2	0.34

TABLE-5
CONDITIONAL STABILITY CONSTANT OF SUBSTITUTED CHALCONES AND ISOXAZOLINES

System	K	log K
Cu(II)-Ligand no. 1	0.1086×10^3	2.0347
Cu(II)-Ligand no. 2	0.0628×10^3	1.7253
Cu(II)-Ligand no. 3	0.8356×10^3	1.9216
Cu(II)-Ligand no. 4	0.0628×10^3	1.7982

TABLE-6
METAL-LIGAND STABILITY CONSTANTS OF COMPLEXES OF 0.1 M IONIC STRENGTH

System	Spectrophotometrically		Potentiometrically	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Cu(II)-Ligand no. 1	5.4012	5.0971	5.4941	5.1538
Cu(II)-Ligand no. 2	4.6501	4.4941	4.6946	4.5337
Cu(II)-Ligand no. 3	5.1128	4.8070	5.946	4.7538
Cu(II)-Ligand no. 4	4.7521	4.1912	4.7096	4.2155

The plots of extension co-efficient against pH at 550 nm and 580 nm were constructed. It showed that 1 : 1 complex is present between pH 2.0 to 3.0 and 1 : 2 complex is present between pH 3.02 to 4.0. The n values were calculated by the procedure given by McBryde[11] and the formation curves were constructed. The $\log K_1$ and $\log K_2$ values (first and second metal-ligand stability constants) were obtained by pointwise calculation method. The values of $\log K_1$ and $\log K_2$ obtained by spectrophotometric and potentiometric measurements are presented in Table-6. It is observed from Table-6, that the values obtained from both the techniques are in good agreement.

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