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Spectrophotometric Determination of Manganese by Biologically Active 5-Chloro-2,4-Dihydroxy Butyrophenone Oxime

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ABSTRACT

5-Chloro-2,4-Dihydroxy Butyrophenone oxime (CDHBO) has been successfully employed as a reagent for spectrophotometric determination for Mn(II) at pH range 7.0 to 11.0 in chloroform medium. The composition of the complex 1:2 (metal:ligand) has been confirm by job's method for continuous variation, Yoe & jones mole ratio method & slope ratio method. The stability constant of the complex is found to be 3.94×10^7. The dark brown coloured complex obeys Beer's law over the concentration range1 to 10 ppm for Mn(II) ion. The complex has molar absorptivity 6.0×10^3 $mol^{-1} cm^{-1}$. While their sensitivity is 0.009 µg Mn/cm^2.Limits of interference due to the presence of foreign ions in the spectrophotometric determination has also been determined. The standard free energy of the complex is 10.442 Kcal/mole at 30°C.

The complex is stable for one week, CDHBO has also been found to give quite satisfactory results for Mn(II) present in synthetic mixtures. The antimicrobial activity of CDHBO and Mn-CDHBO complex have also been calculated.

Key words: Spectrophotometry, Manganese, Biologically active compounds.

INTRODUCTION

A number of reagents are known for spectrophotometric and complexometric determination of Mn(II) and other transition metal ions[1-5]. The present communication deals with the spectrophotometric determination of Mn(II) with CDHBO & compare their biological behaviour with standard drug.

EXPERIMENTAL

Standard stock solution (0.1M) of Mn(II) has been prepared by dissolving appropriate amount of $MnCl_2$ (AR) in double distilled water. The amount of Mn(II) in stock solution was determined by standard method[6].

Preparation of 5-Chloro-2,4-Dihydroxy Butyrophenone oxime (CDHBO)

2,4- Dihydroxy butyrophenone is prepared by standard method.7,8 5-chloro-2,4-Dihydroxy butyrophenone is prepared by passing dry chlorine gas in ethanolic solution of 2,4-dihydroxy butyrophenone (mp 95°C).Oxime of CDHB has been prepared by refluxing CDHB with hydroxyl amine hydrochloride in the presence of sodium acetate in ethanol medium for 2 hrs. The product

separated on concentration and subsequent dilution and recrystallised from ethanol in to colourless needle like crystals (mp130°C)with m.w. 229.5 gm (calcd for $C_{10}H_{12}NO_3Cl$).The structure of the compound was confirm by elemental analysis. IR spectra, NMR spectra and Mass spectra.

Preparation of Mn(II) -CDHBO complex and selection of solvent

The metal ion solution was treated with an ethanolic solution of CHDBO and the mixture was digested on a water bath for about three hours. Mn(II) form dark-brown coloured complex in the pH range 8.5-9.5 respectively. The product was filtered, washed first with warm water and than with 20% ethanol and finally dried in vacuum desiccator at room temperature.

Apparatus

Systronics UV/VIS spectrophotometer (model-118) was used for absorbance measurement & systronic pH meter (model 335) for pH measurement.

RESULTS AND DISCUSSION

Selection of optimum wavelength & pH

The formation of Mn(II) complex with CDHBO & their stability are depend on the pH of solution. While absorbance is depend upon the wavelength.

The method of Vosburg and cooper showed the formation of only one complex having λmax at 405 nm.The absorbance of complex formation was measured at room temperature (300 K) at regular intervals of time up to two week & also different temperature varies from 300K to 325K. The results show that complex is stable for one week & upto 318K without change of absorbance.

The Mn(II) complex exhibit maximum & almost constant absorbance in the pH range 7.0 to 11.0.(Table 2). The subsequent studies were, therefore, carried out at pH 9.5. It was also found that a 15 fold excess of the reagent was necessary to attain the maximum colour intensity.

Table 1: Vosburg and cooper's method for Mn(II) and CDHBO

Concentration of Mn(II)= CDHBO = 1.0×10^{-2} M
Total Volume = 16.0 ml

Wave length	Ratio of Metal to ligand			
(nm)	1:1 OD	1:2 OD	1:3 OD	1:4 OD
405	0.690	0.880	0.890	0.490
410	0.660	0.860	0.870	0.410
420	0.620	0.830	0.860	0.370
430	0.530	0.750	0.830	0.310
440	0.495	0.620	0.770	0.260
450	0.390	0.490	0.670	0.230
460	0.360	0.425	0.580	0.205
480	0.310	0.350	0.470	0.180
500	0.230	0.310	0.380	0.160
520	0.195	0.275	0.320	0.140
540	0.180	0.230	0.290	0.120
560	0.170	0.220	0.270	0.110
580	.160	0.160	0.270	0.110
Metal (ml)	6.0	4.0	3.0	8.0
Ligand (ml)	6.0	8.0	9.0	4.0
Fig. 4.33	A	B	C	D

Reproducibility

Absorbance measurements of a set of six solution prepared in a similar way & have the same concentration of all the reagents show that the reproducibility of measurements are quite good with standard deviation ± 0.432 i.e. 0.26 %.

Stoichiometry and stability constant of the complex

Results of yoe and jones mole ratio method9, slope ratio method10 and job's method of continuous variation11 establish the formation of 1:2 (metal: ligand) complex. (Fig 2,3)

The stability constant of the complex was calculated from the following relationship using mole ratio method. (Table 3)

$$\alpha = \frac{Em - Es}{Em}, \quad K = \frac{1-\alpha}{(m\alpha c)^m \times (n\alpha c)^n},$$

Came to be 3.94 x107. The value of the standard free energy of the formation of complex from the expression $\Delta G = -2.303\ RT \log K$, came to be 10.442 Kcal/ mol at 30°C.

Validity of Beer's law and optimum concentration range

It was observed that the Beer's law is obeyed in the concentration range 1-10 ppm of Mn(II). The optimum concentration range for determination of Mn(II) in solution as deduced from Ringbom plot 12. From the slope ratio curves the molecular extinction coefficient of the complex is 6.0 $x10^3$ while the value of photometric sensitivity as per sendell's scale is found to be 0.009 µgMn/cm^2

Table 2: Effect of pH on the absorbance of Mn(II)-CDHBO at 405 nm

Concentration of Mn(II)=CDHBO	=	1.0×10^{-3} M
Volume of Mn(II) Solution	=	2.0 ml
Volume of CDHBO Solution	=	4.0 ml
Total Volume	=	8.0 ml

pH	O.D	pH	O.D
5.0	0.090	9.0	0.320
6.0	0.180	9.5	0.320
7.0	0.300	10.0	0.340
8.0	0.305	10.5	0.340
8.5	0.310	11.0	0.340

Effect of foreign ions

It was observed that at 5 ppm of Mn(II), 2000 ppm of Cl^-,SO_4^{2-} & CH_3COO^-,1200 ppm of

Table 3: Composition of the Mn(II) CDHBO complex by mole ratio method at 405 nm and ph 9.5

Concentration of Mn(II) Solution	=	2.0×10^{-3} M
Concentration of CDHBOX Solution	=	8.0×10^{-3} M
Constant Volume of Mn(II) Solution	=	1.0 ml
Total Volume	=	25.0 ml
Ionic strength	=	0.1M $NaClO_4$

Volume of CDHBO Solution (ml)	OD	Volume of CDHBO Solution (ml)	OD
0.5	0.195	5.0	0.610
1.0	0.290	6.0	0.630
1.5	0.360	7.0	0.640
2.0	0.410	8.0	0.660
3.0	0.500	9.0	0.660
4.0	0.560	10.0	0.660

Table 4: Analysis of Manganese in various sample

Sample	Mn taken µg	Mn found µg	Absor-bance	Relative error
Synthetic	140	0.410	154.5	
Mixture		0.400	149.3	
No.1		0.428	157.4	0.78
		Avg.	153.7	
Synthetic	110	0.300	112.6	
Mixture		0.316	110.1	
No.2		0.324	113.4	0.81
		Avg.	108.7	
Synthetic	216	0.539	212.3	
Mixture		0.537	219.6	
No. 3		0.542	221.6	0.83
		Avg.	217.8	

NH_4^+, K^+,Na^+, NO_3^-,Br^- and I^-: 850 ppm of SO_3^{-2} & NO_2^-; 500 ppm of Ca^{2+}, Ba^{2+},Sr^{2+}, tartarate & citrate; 200 ppm of Zn^{2+},Cd^{2+} and Be^{2+} could be tolerated. However Cu^{2+}, Pd^{2+}, Co^{2+}, Fe^{3+} & UO_2^{2+} interfered seriously.

A limit of 2.0% change in the absorbance was observed as the limiting concentration.

Determination of Manganese from different samples

The usefulness of the reagent in estimation of manganese was determined from various samples of Mn(II) concentration having different concentration. The sample mixture containing manganese metal were taken for spectrophotometric analysis at different wavelength. The result are given in table (IV)

Analysis

The extracted complex was concentrate & crystallized in desiccator. The elemental analysis of the complex shows metal:ligand (M:L) ratio to be 1:2

Founed	C 46.82	H 4.25	H 5.40	Mn 10.80	Cl 13.90
Calculated	C 46.87	H 4.29	H 5.47	Mn 10.47	Cl 13.86

The IR spectra of CDHBO and complex revealed that the –OH (Stretch) band at 3320 cm^{-1} for the CDHBO disappears during complexation .i.e. complex formation takes place through the N of oximino group and oxygen of the hydroxyl group. The general composition of the complex is $(C_{10}H_{11}NO_3Cl)_2Mn$

Antimicrobial activity

CDHBO & Mn-CDHBO were screened for their antibacterial activity against E.Coli & antifungal activity against Alternaria Alternata using agar diffusion[13] method & dry weight increased method[14]. The results indicate that CHDBO & its Mn(II) complex exhibit more antimicrobial activity with

Table 5: Fungicidal screening data of CDHB,it's derivatives and metal chelates of CDHBO against alternaria alternata at varying concentrations

Test Solution	Average % inhibition after 168 hrs growth of the fungus							
	0.01% Conc.		0.02% Conc.		0.04% Conc.		0.05% Conc.	
	Weight	% inhi bition	Weight	% inhi bition	Weight	% inhi bition	Weight	% inhi bition
Control	1.036	-	1.038	-	1.042	-	1.046	-
Drug(Fluconazole)	1.027	0.85	1.026	0.97	1.03	1.10	0.992	1.25
CDHBO	0.718	30.63	0.589	43.23	0.544	47.76	0.500	52.18
CDHBO-Mn(II)	0.446	56.92	30.5	70.58	0.206	80.16	0.146	85.93

Table 6: Antibacterial activity data of CDHB, it's derivativves and metal chelates of CDHBO against e coli at varying concentration

Test Solution	Inhibition Zone (mm)			
	0.15Conc.	0.20 Conc.	0.30 Conc.	0.40 Conc.
Control	-	-	-	-
Drug				
CHDBO			6.0	8.2
CHDBO-Mn(II)				7.2

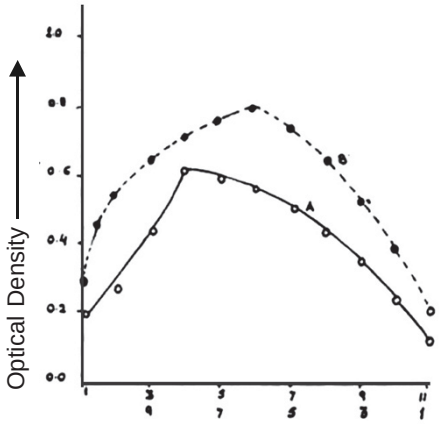
respect to standard drug. (Table 5-6 & Fig. 4-5).

Mode of action

Antimicrobes exert their action in the different ways

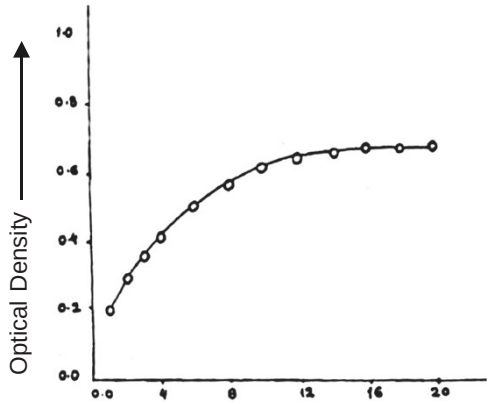
1. Inhibitors of cell wall synthesis.
2. Inhibition of cell membrane
3. Inhibition of Biosynthesis (i.e. production of purines, pyrimidine,Amino acid, Vitamins, Protien, RNA, DNA)
4. Inhibitors of energy production (inhibit the respiration or by uncoupling of oxidative phosphorylation (Disruption the metabolic activities.)

The studies demonstrated that chelation can increase antimicrobial activities than ligand. It has been suggested that metal chelation reduced polarity of metal ion 15 mainly because of the partial shairing of its positive charge with the donor group and possibility the d-electron delocalization occurring with in the whole chelate ring system formed during coordination. This process of chelation thus increase the lipophilic nature of the central metal atom which in turn favours its permeation through the lipoid layer of the membrane[16].



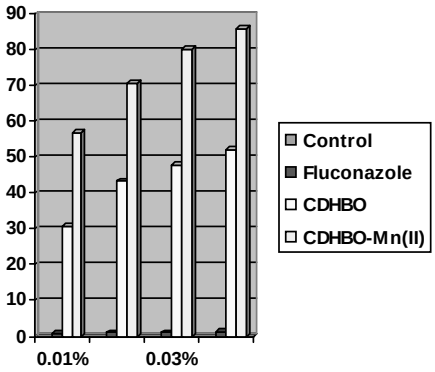
Composition of the Mn(II) - CDHBOX Complex by Job's Method

Fig. 1:



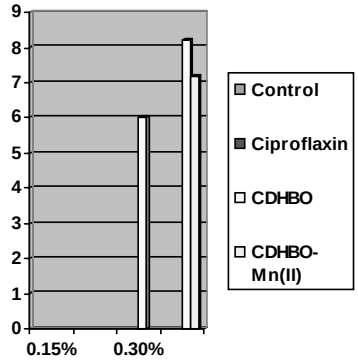
Mole of Reagent / Mole of Mn(II) →
Composition of the Mn(II) - CDHBOX Complex by Mole Ratio Method

Fig. 2:



Conc.

Fig. 3: Effect of concentrations of CDHBO & Mn(II) CDHBO complex on its antifungal potential



Conc.

Fig. 4: Effect of concentration of CDHBO & Mn(II) CDHBO complex on its antibacterial Potential

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