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Thermodynamic and Biological Studies of Some Bivalent Metal complexes with 2,4-Dihydroxy butyrophenone Oxime (DHBOX)

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ABSTRACT

The 2, 4 di-hydroxy butyrophenone Oxime (DHBOX) behaved as mono protic acid and proton was replaced by the metal ion during complex formation & two type of complexes viz 1:1 and 1:2 in the system. The stability constant of DHBOX with bivalent metal ion was calculated. The order of stability constant was in the order Cu(II)>Ni(II)>Mn(II) which is in the agreement with the Irving Williams order. The values of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for ligand were calculated at different temperature.
The effect of ionic strength and temperature on stability constant were also studied.

The antifungal activity and antibacterial activity of different concentration of test compounds were measured by determining the growth of test fungi by dry weight increase method and by agar diffusion method against alternaria alternate & E. coli. The order of antimicrobial effect was observed the following order Cu(II)>Ni(II)>Mn(II).

Key words: Thermodynamic and Biological study, DHBOX

INTRODUCTION

The nitrogen, sulpher donar compounds like oxime, semicarbazide, thiosemicarbazide have significance due to their wide application in industries, medicine, detection and determination of various metal ions[1,2]. The different type of phenones and their oximes have aroused considerable interest as regard to their chelating ability with transition metal ions[3-8]. Which are used as antiseptic[9], germicide[10], anthelmintics[11], analgesic[12], antituberculosis[13] and shows antibacterial, antifungal[14] and antiviral activity[15].

It has been established that the above compound exhibits increased activity in the form of their metal chelates. The structure capable of providing metal chelates may, therefore be provided more potential. Besides their medicinal and biological activities, o- hydroxyl phenones, their derivatives and metal complexes have also been reported as excellent analytical reagent[16].

The present communication deals with the thermodynamic studies of Mn(II),Ni(II),Cu(II) complexes with 2,4-Dihydroxy butyrophenone oxime at 27 ± 0.2º in 75 % (v/v) dioxane water medium at different ionic strength and at different temperature. The antifungal and antibacterial studies of ligand and their complex with Cu(II), Ni(II),Mn(II) is also calculated by using standard methods.

EXPERIMENTAL

The ligand (DHBOX) was prepared by standard method. The following sets of solution were titrated against standard carbonate free sodium hydroxide solution (0.05M) (I),0.05M HClO4 (II)(I) + 0.01 DHBOX and (III) (II) + 0.08 M Metal ion.

The apparent volume of 75% dioxane + 25 % water mixture (V/V) was multiplied by appropriate correction factor[17] to obtain the real volume. Ionic strengths of 0.1, 0.05 and 0.01M were maintained by adding required amount of NaClO4. The pH measurements were made on a systronic 335 digital pH meter and corrected by using Van Uiteret and Hass equation[18]. The value of n, nH and pL were calculated by using standard equations[19]. The log KH values was obtained from the proton ligand formation

Curve (plot between nH and pH and the formation constant of metal complexes were obtained from formation curves (plot between n and pL). The thermodynamic formation constants (Table-1) were obtained by extrapolation of the observed formation constants to zero ionic strength on the graph between log of the stability constant and μ, where μ is ionic strength.

The valves of change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for ligand were calculated at three different temperature at μ=0.1 NaClO4 in 75% (V/V) water-dioxane medium (Table-2) using the following equations.

$\Delta G = -2.303\ RT \log K\mu = 0$

$\Delta H = 2.303\ R \times (T2 \times T1/T2 - T1)(\log K'' - \log K')$

and

$\Delta S = 2.303 \log K + \Delta H/T$

The values of pKmH, θ and ΔH were obtained by the following equations

$pKH - pKmH = C(t - 0)^2$ and $\Delta H = 2.303 \times 10^{-4}\ RT^2 (t - \theta)$

Where, pKH= -logKH at t °c, pKmH= minimum pKH at 0 °c and C=constant ($5 \times 10^{-1} deg^{-2}$).

The antifungal activity and antibacterial activity of different concentration of test compounds were measured by determining the growth of test fungi by dry weight increase method[14] and by agar diffusion method. The test organism were alternaria alternate which was screened in vitro Richard's liquid medium. The percentage of inhibition was also calculated (Table-3), while antibacterial activity was calculated against E.Coli (Table-4).

RESULT AND DISCUSSION

The ligand (DHBOX) behaved as a mono protic acid due to deprotonation of the phenolic OH group ortho to the keto group from which the proton was replaced by the metal ions during complex formation. This was evident from the fact that the metal titration curves were well separated from the ligand titration curves.

The values of n >2 were not obtained in any case showing thereby the formation of only type of complexes, viz 1:1 and 1:2 in the System. In the complexes of Mn(II), the value of n is always <1, which is due to hydrolysis, in such cases only log K1 values have been calculated. In the case of Ni(II), the values of ν- were < 1.5, hence the log K_2 values were calculated using the equation

$2\log K = \log K1 + \log K2$

where logK= pL at n =1.0. It has been found that logK1 > logK2 in all the cases studied. The order of stability constants of bivalent metal complexes was found Cu(II)>Ni(II)>Mn(II) which is in the agreement with the Irving-Williams order[20].

The more stability of Cu- complex in comparison to that of Ni complex may be attributed to the difference in their respective configuraton[21]. it is probable that Cu (II) forms planar chelates, while Ni (II) forms tetrahedral or preferable octahedral chelates.

The greater stability of Zn (II) chelates in comparison to those of Ni(II) may be attributed to the electron delocalization of 3d orbitals of Zn(II) through interaction with oxygen orbitals not taking part in π- bonding and the π- orbitals of benzene rings.

The value of log βn and log K^H decreases with the increase of ionic strength. According to Huckle, the activity of a metal ion for its interaction

with other molecular species decreases with the increase in the ionic strength of the medium. Accordingly, the formation constant would decrease with increase in the ionic strength of the medium, which in agreement with the observation of Debye[22]. The Protonation constant of ligand and stability constants of metal complexes decrease with the increase in temperature.

The Screening results indicate that fungal and bacterial growth was inhibited on addition of chemicals at varying concentrations. However, the ligand as well as the metal complexes showed increased activity at higher concentration than at lower concentration for a given fungus and bacteria.

The activity showed a gradual change with change of metal ion in the complexes and observed the following order.

Cu(II)>Ni(II)>Mn(II)

Thus,Mn(II)- complex is least toxic while Cu(II) complex has the maximum activity. This may attribute to the fact that copper itself is a toxic element and the increase in toxicity in the metal chelates is probably either due to the faster diffusion of the chelates as a whole through the cell membrane23 which may block the enzymatic activity of the cell or else it may catalyse toxic reactions among cellular constituents[24-26]

Antibacterial agent exert their action on the pathogen in the following ways.

1. Inhibitors of cell wall synthesis.
2. Inhibitors of Bio-synthesis(i.e.inhibit production of purines,pyrimidine,AA, Vitamins,Protein, RNA,DNA).
3. Inhibitors of energy production (Inhibit the respiration or by uncoupling of oxidative phosphorylation (Disruption the metabolic activities).The experimental data demonstrated that chelation can increase antimicrobial activity than ligand. It has been suggested that metal chelation reduced polarity of metal ion mainly because of the partial sharing of its positive charge with the donar group & possibility of delocalization of d-election occuring 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 lipid layer of the membrane.

Table- 1: Proton-Ligand and Metal-Ligand Constants withDHBOX at 27 ± 0.2° in 75% (V/V) DIOXANE medium at different ionic strengths

	μ= 0.1M			μ=0.05M			μ=0.01M		
	logK1	logK2	logβn	logK1	logK2	logβn	logK1	logK2	logβn
H+	-	11.70	11.70	11.96	-	11.96	12.16	-	12.16
Cu(II)	11.36	7.62	15.72	8.00	7.65	15.87	8.68	7.32	15.0
Ni(II)	6.15	5.40	11.65	5.94	5.92	11.52	6.50	5.71	12.30
Mn(II)	5.42	-	5.42	5.90	-	5.90	6.10	-	6.10

Table 2 :Protonation Constants and the Thermodynamic Parameters at Different Temperature for DHBOX at μ = 0.05M

Temperature °K	PK1H	- ΔGK Cal/mole	- ΔHKcal/mole	ΔSCal/deg/mole	0°C	PK_mH
293	12	16.11	-	26.80-	-	
300	11.86	16.30	8.26	26.82	205	10.10
305	11.70	16.51	-	26.81	-	-

Table- 3:Fungicidal screening data of DHBOX and their metal chelates against Alternaria Alternate at varying concentration.

Test. solution	0.10% cons.		0.20% cons.		0.30% cons.		0.40% cons.	
	Weight	% inhi biton	Weight	% inhi biton	Weight	% inhi biton	Weight	%inhi bition
Control	1.20	-	1.20	-	1.20	-	1.20	-
Fluconazole	1.1664	2.8	1.143	4.78	1.12212	6.49	1.095	8.75
HMBOX	1.1604	3.3	1.134	5.52	1.098	8.49	1.071	10.75
HMBOX-Mn(II)	1.0992	8.4	1.1316	5.52	1.05504	12.08	1.0002	16.65
HMBOX- Ni(II)	1.0632	11.4	1.071	10.78	1.04232	13.14	0.9603	19.88
HMBO- Cu(II)	0.828	31.0	0.98	18.15	0.9273	22.72	0.8712	27.40

Table -4 :Antibacterial Activity data of DHBOX and their metal chelates against E.Coli at varying concentrations.

Test Solution	Inhibition Zone (mm)			
	0.10% Conc.	0.20% Conc.	0.30% Conc.	0.40% Conc.
Control	-	-	-	-
Ciproflaxacin				5.64
HMBOX	-	-	4.24	6.82
HMBOX-Mn(II)	-	4.2	4.85	7.18
HMBOX-Ni(II)	-	6.6	7.16	10.40
HMBOX-Cu(II)	-	7.7	7.94	11.12

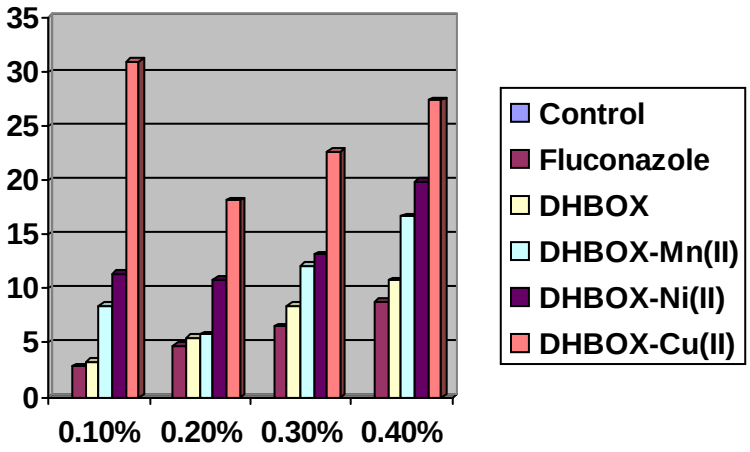

Fig. 1: Fungicidal Screening data of DHBOX and their metal chelates against Alternaria Alternate at varying concentration.

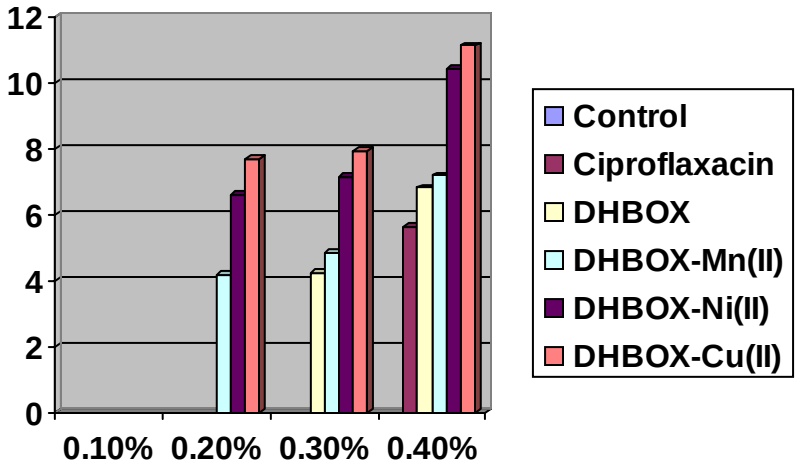

Fig.2 : Antibacterial Activity data of DHBOX and their metal chelates against E.Coli at varying concentration.

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