IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Assessment Of Standard Change In Entropy Accompanying Complexation Of Bromobenzoylthioacetophenone With Cu, Ni, Zn & Cd.

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ABSTRACT

The complexes of para-Bromobenzoylthioacetophenone have good therapeutic applications. The Overall stability constants of bivalent complexes of Copper, Nickel, Zinc and Cadmium with the said ligand have been determined potentiometrically at three different temperatures using Calvin-Bjerrum potentiometric technique as modified by Irving and Rossotti. From a knowledge of overall stability constant data, standard change in Free energy and Enthalpy were determined with the help of appropriate methods. Finally, the Standard Change in Entropy (ΔS^0) accompanying the above complexations were evaluated using the thermodynamic relation, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. From the data obtained, Standard change in Entropy have been properly discussed.

Key-Words: Stability Constant, Potentiometric technique, Standard change in Entropy.

INTRODUCTION

Para-bromobenzoylthioacetophenone, the ligand of our research work belongs to Monothic-β-diketone, an orgnic compound. This ligand behaves as a uninegatively charged bidentate ligand after deprotonation through its enol or enethiol form resulting in the formation of a six-membered resonance stabilised ring complex with metal ions. The metal ions taken are Cu, Ni, Zn and Cd all in bivalent state. The structure of the ligand is presented below.

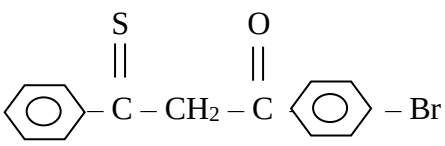


Fig.1: Para-Bromobenzoylthioacetophenon

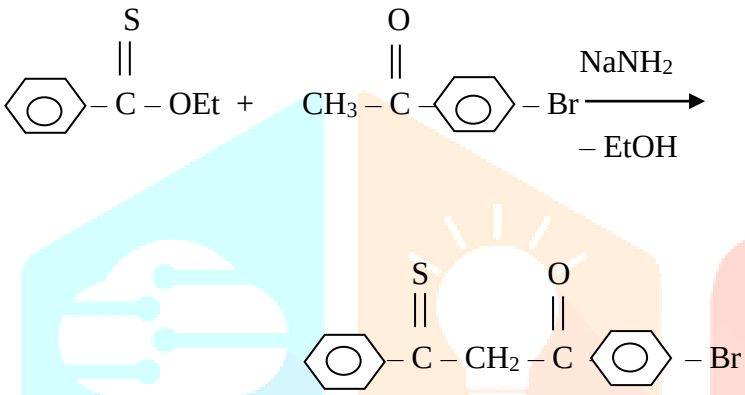
However, no attempt has been made so far to study the solution equilibria of the said ligand and its derived metal complexes with the metal ions taken as also the standard charge in Entropy

accompanying the above complexations. This can help to understand the chelating ability of the ligand as also to know the changes taking place in Entropy associated with above complx formation.

In the present communication, we report the overall stability constants of p-bromobenzoylthioncatophenone with Copper, Nickel, Zinc and Cadmium (all bivalent) in 75% aqueous dioxan at 10°C, 20°C and 30°C at a fixed ionic strength of 0.1M KCl as determined by Calvin-Bjerrum's pH-metric technique as modified by Irving and Rossotti as well as changes taking place in thermodynamic factors associated with the above complexation.

METHODOLOGY

Para-Bromobenzoylthioacetophenore, the ligand of the the present work was synthesised by Claisen Condensation of o-Ethylthiobenzoate with p-bromoacetophenone as shown below.



p-bromobenzoylthioacetophenone

Primary standard solution of the ligand was prepared in dioxan.[6] Aqueous solutions of bivalent metal chlorides were standardised, KOH solution was prepared in CO_2-free conductivity water and used to standardise HCl solution. KCl solution was prepared in 1:1 dioxan-water medium and used to maintain the desired strength. The temperatures were kept constant at 10°C, 20°C and 30°C for the experimental condition.

Procedure

Following three mixtures were prepared for potentiometric titration.

(i) 5 ml 0.4 M HCl + 5 ml M KCl

(ii) Mixture (i) + 5 ml 0.02 M Ligand solution, and

(iii) Mixture (ii) + 5 ml 0.004 M Metal ion solution.

Total volume in each case was kept 50 ml so that the volume of dioxan remained 70%, and the ionic strength was kept at 0.1 M (KCl). The mixtures were titrated against 0.2 M KOH solution, and the pH was measured in oxygen-free nitrogen atmosphere. The pH-meter readings (B-values) and the volume of alkali added were plotted in each case and referred to as (i) Acid (ii) Ligand, and (iii) Complex Titration curves respectively[3,4,6,7.]

From the acid and ligand titration curves, values of $\bar{n}_A$ at various B-values were calculated using appropriate equation. A plot of $\bar{n}_A$ vs B gave Formation Curve of Ligand-Proton complex. From this curve, pKa values (Protonation Constant) of the ligand was obtained by Half-Integral Method.[5,9] Likewise, values of $\bar{n}$ and pL were calculated from Ligand and Complex titration curves using suitable equations.[6,7,8]

Formation Curves of the Metal-Ligand Complexes were drawn by plotting $\bar{n}$ vs pL for each complex. From these curves, the Stepwise and Overall stability constants for each complex were obtained by Half Integral Method (Log K_1 = pL at $\bar{n}$ = 0.5 and Log K_2 = pL at $\bar{n}$ =1.5). The results obtained are furnished below in Table-1.

TABLE- 1

Stepwise and Overall Stability Constant Data of Complexes formed

[μ= 0.1M KCl; Medium = 75% Aqueous Dioxan (v/v)]

$LogK_I^H = pKa = 10.25$ at 10°C; 10.10 at 20°C & 10.02 at 30°C

Metal Ion	TEMPERATURE								
	10^0C			20^0C			30^0C		
	LogK$_1$	LogK$_2$	Logβ	LogK$_1$	LogK$_2$	Logβ	LogK$_1$	LogK$_2$	Logβ
Cu^{II}	10.69	09.84	20.53	10.55	09.73	20.28	10.47	09.68	20.15
Ni^{II}	10.65	09.65	20.30	10.40	09.54	19.94	10.36	09.47	19.83
Zn^{II}	09.75	08.97	18.72	08.93	08.43	17.36	08.87	08.39	17.26
Cd^{II}	08.99	08.44	17.43	08.88	08.31	17.19	08.72	08.18	16.90

Thus, the Stability order of metal complexes follow the trend: $Cu^{II} > Ni^{II} > Zn^{II} > Cd^{II}$

From the above stability constant data, the standard change in free energy were evaluated by the thermodynamic relation, $\Delta G^0 = -2.303RT \log\beta$. The obtained values are furnished below in Table-2

Table-2

ΔG^0 values of Bivalent Metal Complexes

Metal ions	$-\Delta G^0$ (K Cals/mol)		
	10°C	20°C	30°C
Cu^{++}	26.58	27.19	27.93
Ni^{++}	26.28	26.73	27.49
Zn^{++}	24.24	23.27	23.93
Cd^{++}	22.57	23.04	23.43

For determining standard change in Enthalpy, both Linear Plot Method as well as Gibbs-Helmholtz equation were employed. The data obtained are furnished below in Table-3.

Table - 3

ΔH^0 values of Metal Complexes at 20°C

Metal ions	$-\Delta H^0$ (K Cals/mol)			
	By Linear Plot Method	By Gibbs-Helmholtz eqn.(t=20±1°C)		
		$dT = T_2 - T_1$	$dT = T_3 - T_2$	Average Values
Cu^{++}	7.51	9.32	5.51	7.42
Ni^{++}	9.34	13.55	4.47	9.01
Zn^{++}	18.49	-	3.94	3.94
Cd^{++}	13.06	9.27	11.62	10.45

DETERMINATION OF ΔS^0

The values of Standard Change in Entropy (ΔS^0) were evaluated from the data obtained for ΔG^0 (Table-2) and ΔH^0 (Table-3). Using these data, the Standard change in Entropy was calculated through the well known Thermodynamic relation: $\Delta G^0 = \Delta H^0 - \Delta S^0$. The values of ΔS^0 obtained are presented below in Table-4.

Table-4

ΔS^0 values of Bivalent Metal Complexes at 20°C

(M=0.1M KCI; Medium 75% Aq. dioxan)

Metal ion	**ΔS^0 (Cals/deg/mol)**		
	Using ΔH^0 by LPM	Using ΔH^0 by G-H eqn. at 20°C	Average values
Cu^{++}	67.17	67.07	67.31
Ni^{++}	59.35	60.47	59.91
Zn^{++}	16.31	65.97	41.14
Cd^{++}	34.06	42.96	34.51

RESULTS & DISCUSSION

From the various data obtained, furnished in different tables, it is obvious that like Stability Order (Table-1), the decrease in free energy change follows the same trend: **Cu(II) > Ni(II) > Zn(II)> Cd(II).** This reflects that the complexes formed are free energy stabilised. The average values of ΔH^0 obtained from both Linear plot Method and Gibbs-Helmholtz equation show a successive increase for all the complexes except that of Zinc which suggests that Zinc has altogether different behaviour towards the ligand used, Zinc being a pseudo transition metal.

So far as Standard Change in Entropy is concerned, the same pattern is observed. From table 4 containing values of ΔS^0 at 20°C, it is obvious that complex of copper is highly stabilized having maximum disordesness. The average values of ΔS^0 for the complexes of Cu, Ni, Zn and Cd are respectively 67.31, 59.91, 4114 and 34.51 cals/deg/mol. The values of ΔS^0 so obtained clearly support the stability order: **Cu(II) > Ni(II) > Zn(II) > Cd(II)**

CONCLUSION

In the present investigation, we find that all the thermodynamic factors conform the stability order (Table-1) of the complexes formed. So far as values of ΔS^0 are concerned, the Standard Change in Entropy goes on decreasing from Cu- to Cd-complex. Thus, complex of copper has highest stability because the greater the disorderness, the greater will be the value of entropy, and hence greater will be the stability of the complex formed.[8,11,15]

Thus, all the complexes formed are entropy stabilised. From the data obtained, it reflects that Standard Change in Entropy supporting the Stability order (Tabl.-1) follow the same trend: **Cu(II) > Ni(II) > Zn (II) > Cd(II).**

DECLARATION

It is declared that all ethical guidelines have been properly followed during this work, and there is no conflict of interest with anyone.

ACKNOWLEDGEMENT

The authors are thankful to H.O.D., University Department of Chemistry, J. P. University, Chapra for providing laboratory facilities.

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