Evaluation of Standard Changes in Enthalpy During Complex Formation of Mn(II), Ni(II), Cd(II) and Hg(II) with p-fluorobenzoylthioacetophenone

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ABSTRACT

The stability constant values of the complexes of p-fluorobenzoylthioacetophenone with bivalent manganese, nickel, cadmium and mercury at different temperatures viz. 283K, 293K and 303K have been determined using Calvin-Bjerrum's pH titration technique as adopted by Irving and Rossotti. Standard change in free energy at desired temperatures were evaluated with the help of data of overall stability constants using the thermodynamic expression, $\Delta G° = -2.303\ RT\ Log\ \beta$. The standard changes in enthalpy associated with the complex formation reactions were evaluated with the help of Isobar equation. The standard enthalpy change was also calculated by using Gibbs-Helmholtz equation. From values obtained, the standard changes in enthalpy associated with the above complex formation have been thoroughly discussed.

Keywords: Enthalpy, Monothio-β-diketones, Overall Stability Constant, p-fluorobenzoylthioacetophenone, Solution Equilibria

INTRODUCTION

p-fluorobenzoylthioacetophenone was chosen as ligand for complexation with bivalent manganese, nickel, cadmium and mercury. This ligand belongs to monothio-β-diketone[1,2,3] class of compounds. It acts as a bidentate chelating ligand by deprotonation through its enol or enethiol[4,5,6] form and produces a stable six membered chelate[7].
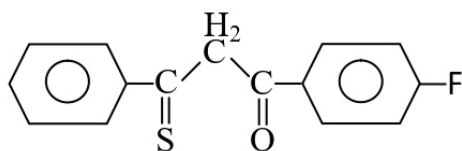

Figure 1: p-fluorobenzoylthioacetophenone

Attempts were not made as yet to study the solution equilibria of this ligand and its derived metal chelates as also standard change in enthalpy accompanying the complexations – a work which will help to know the contribution of standard change in associated enthalpy, a significant thermodynamic factor towards said complexation.

Through present communication we report here the overall stability constants[8,9,10] of the complexes of p-fluorobenzoylthioacetophenone with Mn, Ni, Cd and Hg (all bivalent) at 283K, 293K and 303K with assessment of thermodynamic factors namely (ΔG°) standard changes in free energy and (ΔH°) standard changes in enthalpy accompanying the above complexations. pH-metric titration technique of Calvin-Bjerrum[11,12] as employed by Irving and Rossotti[13] was used to determine the overall stability constants of the complexes.

MATERIALS AND METHODS

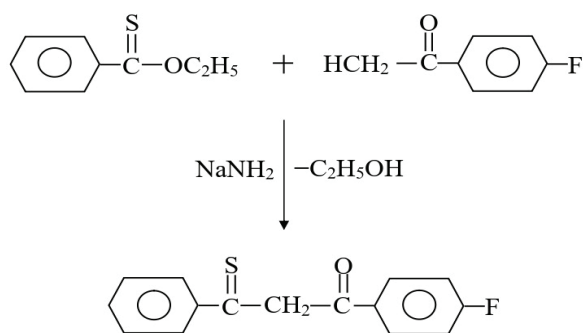p-fluorobenzoylthioacetophenone was prepared through Claisen condensation as shown below.

Figure 2: Synthesis of p-fluorobenzoylthioacetophenone

The following mixtures were prepared for the experiments to be performed.

i) 5 ml 0.4 M hydrochloric acid + 5 ml M KCl

ii) Mixture (i) + 5 ml 0.02 M solution of ligand

iii) Mixture (ii) + 5ml 0.004 M solution of metal chlorides

Total volume of 50 ml was kept in each experiment so that dioxan[14,15] volume remained 70% while ionic strength was kept at 0.1 M potassium chloride . The mixtures were titrated with 0.2 M potassium hydroxide solution and the measurement of pH was done in in oxygen−free nitrogen atmosphere. A graph of B- values against the volume of alkali added was plotted in each case and designated as (1) Acid, (2) Ligand and (3) Complex Titration Curves respectively.

Values of $\bar{n}_A$ at different B-values were found from acid and ligand titration curves via appropriate equation. Formation Curve of the Ligand-Proton Complex was obtained by plotting of $\bar{n}_A$ versus B. From these graphs, the pKa value of ligand was evaluated using half-Integral method[12,16], (Log $K_1^H = pKa = B$ at $\bar{n}_A = 0.5$).

This was further validated by linear plot of Log $\bar{n}_A/(1-\bar{n}_A)$ versus B. The values of $\bar{n}$ versus pL were obtained from the ligand and complex titration curves through appropriate equations. Formation curves of metal-ligand complexes were found by plotting a graph of $\bar{n}$ against pL for each of the complexes formed. The stepwise formation constants of each metal complex (Log K_1 and Log K_2) were found by half integral method (HIM). Thus, Log $K_1 = pL$ at $\bar{n} = 0.5$ was obtained. In the same manner, Log $K_2 = pL$ at $\bar{n} = 1.5$ was obtained. Since, the difference between the values of Log K_1 and Log K_2 values was too small, it was refined by least square treatment[16] (LST).

RESULTS AND DISCUSSION

From the experiments, the data of stepwise and overall stability constant obtained are arranged below.

**Table-1: Stability Constant Data of Metal Complexes at different temperatures**

Protonation constant values of ligand, pKa= 10.77 (283K), 10.60 (293K) and 10.52 (303K)

Metal Ions	Temperatures								
	283K			293K			303K		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Ni^{2+}	10.47	09.43	19.90	10.21	09.38	19.59	10.18	09.31	19.49
Mn^{2+}	09.57	08.63	17.95	09.18	08.52	17.70	09.03	08.40	17.43
Cd^{2+}	08.94	08.35	17.29	08.76	08.16	16.92	08.59	08.05	16.64
Hg^{2+}	08.72	08.26	16.98	08.83	08.06	16.69	08.39	07.89	16.28

Table-2 : ΔG° values of Bivalent Metal Complexes at three different temperatures namely 283K, 293K and 303K.

Metal ions	-ΔG°(kcal mol)		
	Temperatures		
	283K	293K	303K
Ni^{2+}	25.77	26.26	27.02
Mn^{2+}	23.24	23.73	24.16
Cd^{2+}	22.39	22.68	23.07
Hg^{2+}	21.98	22.37	22.57

Here, Log K_1 and Log K_2 are stepwise stability constants whereas Log β is overall stability constant. From the above table, it is obvious that the stability constants of metal complexes follow the order:

$$Ni^{II} > Mn^{II} > Cd^{II} > Hg^{II}$$
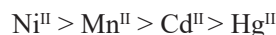
Standard change in Free energy at a particular temperature was evaluated by utilising the thermodynamic relation, ΔG° = −2.303 RT Log β where, the contained terms have the usual meaning.

The Standard change in Enthalpy[17,18] associated with the formation of complex was evaluated using the following isobar equation.

$$\frac{d \ln \beta}{dT} = \frac{\Delta H^0}{RT^2}$$

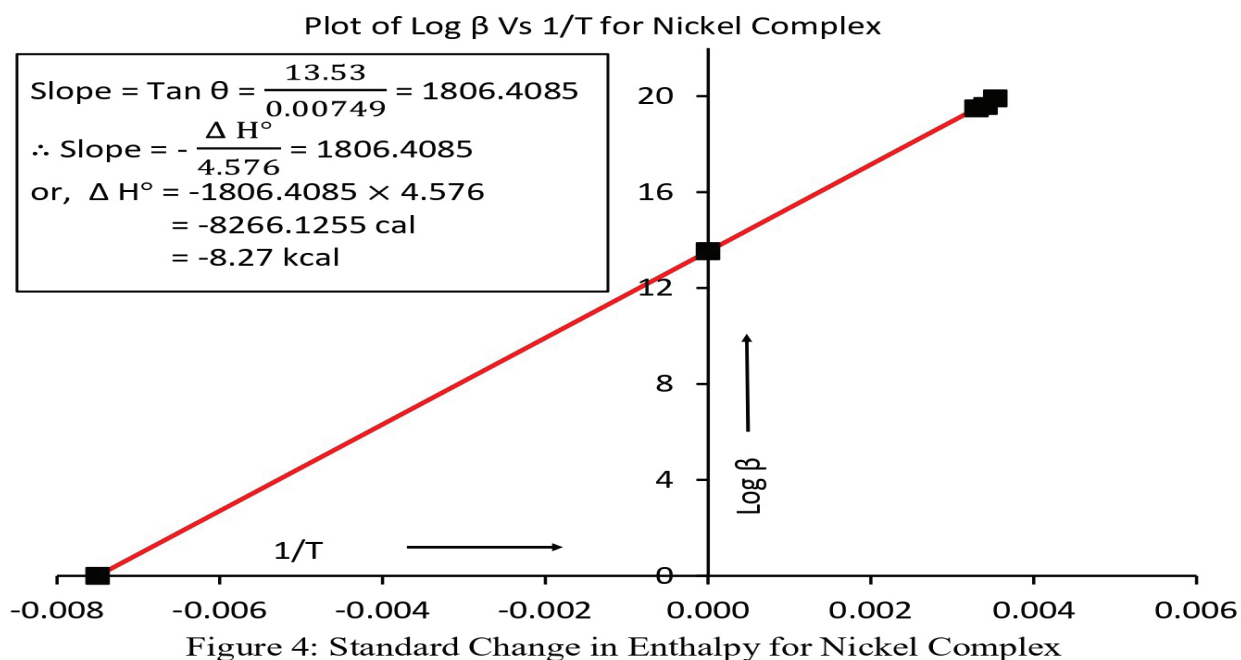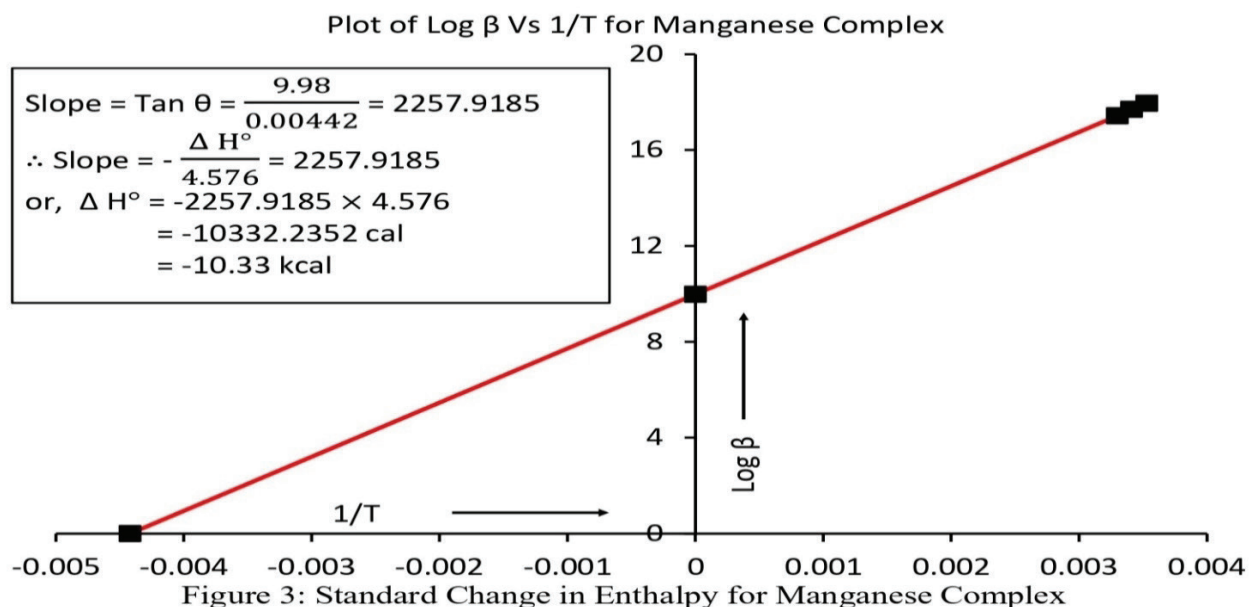The above expression can be put as:

$$\frac{d\left(\log \beta\right)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^0}{2.303R}$$

Putting R = 1.987 cal K^{-1} mol^{-1}, we get

$$\frac{d\left(\log \beta\right)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^0}{4.576}$$

In accordance with the above expression, gradient of a tangent drawn at the point corresponding to any particular temperature on the curve formed by plotting the values of Log β as a function of 1/T should be equal to $\frac{-\Delta H^0}{4.576}$.

The values of $\Delta H°$ was also determined by Gibbs-Helmholtz equation. These values of standard change in enthalpy obtained by plotting Log β versus 1/T (linear plot method) as well as by using Gibbs-Helmholtz equation are furnished below. Related graphs are presented below.
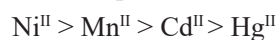

Figure 3: Standard Change in Enthalpy for Manganese Complex

Figure 4: Standard Change in Enthalpy for Nickel Complex

Plot of Log β Vs 1/T for Cadmium Complex

Slope = Tan θ = $\dfrac{7.29}{0.00257}$ = 2836.5758

∴ Slope = - $\dfrac{\Delta H°}{4.576}$ = 2836.5758

or, $\Delta H°$ = -2836.5758 × 4.576
= -12980.1712 cal
= -12.98 kcal

Figure 5: Standard Change in Enthalpy for Cadmium Complex

Plot of Log β Vs 1/T for Mercury Complex

Slope = Tan θ = $\dfrac{6.29}{0.00208}$ = 3024.0384

∴ Slope = - $\dfrac{\Delta H°}{4.576}$ = 3024.0384

or, $\Delta H°$ = -3024.0384 × 4.576
= -13837.9997 cal
= -13.84 kcal

Figure 6: Standard Change in Enthalpy for Mercury Complex

Table-3 Standard change in enthalpy of metal complexes in kcals mol^{-1}.

Metal ions	-ΔH° (kcal mol^{-1})		
	By Linear Plot Method	**By Gibbs- Helmholtz equation at 30 ± 1°C**	**Average values**
Ni^{2+}	8.27	7.94	8.10
Mn^{2+}	10.33	10.25	10.29
Cd^{2+}	12.98	12.71	12.84
Hg^{2+}	13.84	13.72	13.78

## CONCLUSION

In the present investigation, the decrease in standard free energy change at each temperature follows the order:

$$Ni^{II} > Mn^{II} > Cd^{II} > Hg^{II}$$

This is obvious from the data furnished in Table-2. Therefore, the metal complexes formed are free energy stabilized. Linear plot method shows a successive increasing value of standard change in enthalpy from Ni-

complex to Hg-complex. Also, the standard change in enthalpy evaluated by using Gibbs-Helmholtz equation follows the same pattern i.e. it also gives the increasing value of $\Delta H°$ for complexes of nickel to mercury. Their average values also support the same pattern. The negative values of standard change in enthalpy for each metal complex as given in Table-3 implies that the complex formation reactions are exothermic. Therefore, all the metal complexes formed are enthalpy stabilized. Also, from the data furnished in Table-3, it is obvious that the standard change in enthalpy conforming the stability order as listed in Table-1 follow the pattern:
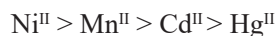
$$Ni^{II} > Mn^{II} > Cd^{II} > Hg^{II}$$

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