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A Study Of Entropy Change Accompanying Complexation Of Fluorobenzoylthioacetophenone With Some Transition Metals

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ABSTRACT

Stepwise and Overall Stability Constants of the complexes of Para–luorobenzoylthioacetophenone, the ligand of the present research work with some bivalent transition metals at different temperatures have been determined potentiometrically using Calvin-Bjerrum potentiometric technique as modified by lrving and Rossotti. From a knowledge of Overall Stability Constants of the complexes formed, Standard changes in some Thermodynamic factors accompanying the above complex formation reaction were determined with the help of appropriate thermodynamic relationships. From the data obtained, Standard Change in Entropy contributing towards said complex formation has been properly discussed.

Key−words: Fluorobenzoylthioacetophenone, Overall Stability Cons- tant, Potentiometric technique, Standard Change in Entropy.

INTRODUCTION

The ligand, p-fluorobenzoylthioacetophenone as shown below was chosen for complexation with bivalent Manganese, Nickel, Cadmium and Mercury. The ligand behaves as uninegatively charged bidentate chelating agent after deprotonation through its enol or enethiol form resulting in the formation of a six-membered resonance stabilized ring complex with metal ions.

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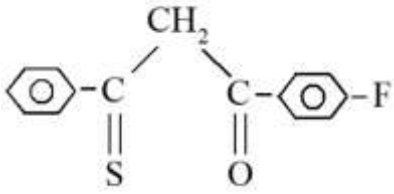

Fig 1: **The Ligand**

However, no attempt appears to have been made to study the solution equilibria of this ligand and its derived metal complexes – a work that can help us to know the effect of Fluorine substituent on the stability of metal complexes formed when compared with those of Benzoylthioacetophenone already reported.[1,2,5.]

In the present communication, we report the Stability Constants of the complexes of p-fluorobenzoylthioacetophenone with said transition metals at different temperatures at a fixed ionic strength of 0.1M KCl by potentiometric technique. Thereafter, using these data, the Standard Change in Entropy accompanying the above complexation has been determined using specific thermodynamic relation.

EXPERIMENTAL

By the reported method[4,6], the ligand was synthesised through Claisen Condensation of o-ethylthiobenzoate with p-fluoroaceto-penone in presence of sodamide, and the product was recrystallized in ethylalcohol, m.pt. 130°C (lit. 129°C)[5,7]. The synthesis is depicted below.

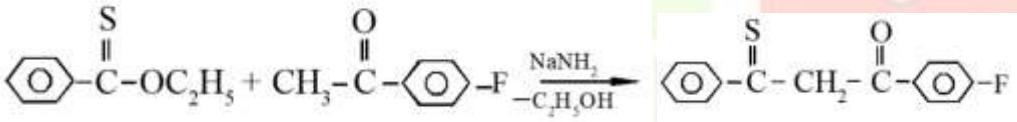

Fig 2: Synthesis of p-Fluorobenzoylthioacetophenone

Primary standard solution of ligand was prepared in dioxan[4]. Aqueous solutions of Metal (II) chlorides were standardized. KOH solution was prepared in CO_2-free conductivity water and used to standardize HCl solution. KCl soulution was prepared in 1:1 dioxan-water medium and was used to maintain the desired ionic strength. The temperatures were maintained constant at 10°C, 20°C and 30°C respectively for three different experiments.

Procedure : The following three mixtures were prepared :-

(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 maintained 50ml such that the volume of dioxan remained 70% and 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 O_2-free nitrogen atmosphere. The B-values (pH-meter readings) and the volume of alkali added was plotted in each case and referred to as (i) Acid (ii) Ligand, and (iii) Complex Titration Curves respectively[1,2,3,5]

From acid and ligand titration curves, $\bar{n}_A$ values at various B-values were calculated using the appropriate equation. A plot of $\bar{n}_A$ against B gave the Formation Curve of Ligand–Proton complex. From this curve, pKa value of ligand or its protonation constant $\left(K_I^H = \frac{1}{Ka}\right)$ was obtained by Half−Integral Method. i.e. Log K_I^H = pKa = B at $\bar{n}_A$ = 0.5.

This was further corroborated by Linear Plot of $\text{Log}\frac{\bar{n}_A}{1-\bar{n}_A}$ versus B.[10,11]

From Ligand and Complex titration curves, the values of $\bar{n}$ and pL were calculated using the appropriate equations.[7,9,10] Formation Curves of the Metal – Ligand Complexes were drawn by plotting $\bar{n}$ vs pL for each complex. From these curves the stepwise stability constants of each metal complex (Log K_1 and Log K_2) were obtained by Half Integral method[8,9,10]. i.e. Log K_1 = pL at $\bar{n}$ = 0.5 and Log K_2 = pL at $\bar{n}$ =1.5. Since the difference between LogK_1 and LogK_2 values was found to be very small, the same were refined by Least Square Treatment, and the results were reported in Table-1.

TABLE- 1.

Stepwise and Overall Stability Constant of Metal Complexes

[μ= 0.1M KCl, Medium : 75% Aq. Dioxan (v/v)]

Log K_I^H = pKa = 10.77 at 10°C; 10.60 at 20°C & 10.52 at 30°C

Metal Ion	TEMPERATURE								
	10 ± 1^0 C			20 ± 1^0 C			30 ± 1^0 C		
	LogK_1	LogK_2	Logβ	LogK_1	LogK_2	Logβ	LogK_1	LogK_2	Logβ
Ni^{II}	10.47	09.43	19.90	10.21	09.38	19.59	10.18	09.31	19.49
Mn^{II}	09.57	08.63	17.95	09.18	08.52	17.70	09.03	08.40	17.43
Cd^{II}	08.94	08.35	17.29	08.76	08.16	16.92	08.59	08.05	16.64
Hg^{II}	08.72	08.26	16.98	08.83	08.06	16.69	08.39	07.89	16.28

Thus, the stability of Metal Complexes follow the trend :

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

Evaluation of ΔG^0 :- The value of standard change in Free energy, (ΔG^0) was calculated using Thermodynamic expression, $\Delta G^0 = -2.303\ RT\ \text{Log}\beta$, where β= Overall Stability constant, T= Temperature, R = Constant. The ΔG^0 values at different temperatures for each metal complex are given in Table 2 below.

TABLE- 2 :

ΔG^0 values of Metal Complexes.

[μ= 0.1M KCl, Medium : 75% Aq. Dioxan (v/v)]

Metal ions	$-\Delta G^0$ (in k Cals/mol)		
	10 ± 1^0 C	20 ± 1^0 C	30 ± 1^0 C
Ni^{II}	25.77	26.26	27.02
Mn^{II}	23.24	23.73	24.16
Cd^{II}	22.39	22.68	23.07
Hg^{II}	21.98	22.37	22.57

Thus, It is obvious that the decrease in standard free energy is higher at higher temperature.

Determination of ΔH^0:The Standard change in Enthalpy accompanying the complex formation was determined by Isobar equation as well as Gibbs–Helmholtz equation. These values of ΔH^0 obtainable from the plot of Logβ vs 1/T (Linear Plot method) using Isobar equation and through Gibbs–Helmholtz are listed in Table-3.

TABLE-3.

ΔH^0 values of Metal complexes at 20^0C.

Metal ions	$-\Delta H^0$ (K Cals mol^{-1})		
	By LPM	By G-H eqn.	Average values
Ni^{++}	8.27	7.94	8.10
Mn^{++}	10.33	10.25	10.29
Cd^{++}	12.98	12.71	12.84
Hg^{++}	13.84	13.72	13.78

EVALUATION OF ΔS^0 (Standard Change in Entropy)

The values of standard change in Entropy were calculated using average value of ΔH^0 through the thermodynamic equantion, $\Delta G^0 = \Delta H^0 - T\Delta S^0$. The required values of ΔG^0 and ΔH^0 are mentioned in Table–2 & 3. The value of ΔS^0 obtained are arranged below in Table-4.

TABLE- 4

ΔS^0 values of Bivalent Metal Complexes using the average value of ΔH^0

Metal ions	ΔS^0 (Cals deg^{-1}. mol^{-1}) at 20^0C
Ni^{++}	61.97
Mn^{++}	45.87
Cd^{++}	33.58
Hg^{++}	29.31

RESULTS & DISCUSSION

From the thermodynamic relation, $-RT\ln\beta = \Delta G^0 = \Delta H^0 - T\Delta S^0$, it is obvious that β increases when ΔG^0 becomes more negative. The value of ΔG^0 becomes more negative when that of ΔS^0 becomes more positive. That is to say, more positive value of ΔS^0 will lead to a more negative value of ΔG^0 and hence a more stable complex will be formed. It is imperative to know that greater the amount of heat released in a reaction, more stable will be the reaction product.

The entropy of a system is a measure of degree of disorderness or randomness of the system. The greater the amount of this disorder produced, the greater will be the value of entropy during the reaction and hence greater will be the stability of Complexes formed.[9,14,15]

In the present investigation, we find that all the Thermodynamic parameters in conformity with the stability order follow the same trend. In case of standard change in Entropy (ΔS^0) for these complexes, we find the same pattern as is followed by Standard Change in Free energy and Enthalpy. From Table - 4 containing ΔS^0 values calculated at 20^0C for these complexes, it is obvious that Nickel complex is much entropy stabilized having maximum disorderness. The values of ΔS^0 clearly support the stability order : **Ni>Mn>Cd>Hg**

Thus, the values of ΔS^0 obtained support the stability order observed in the case of all the four bivalent complexes. For the sake of convenience it is imperative to know here that the values of entropy change in the case of Nickel, Manganese, Cadmium and Mercury are respectively 61.97, 45.87, 33.58 and 29.31 when determined using average value of ΔH^0 obtainable by both Linear Plot Method and Gibbs-Helmholtz equation at 20^0C.

It is noticeable that the increase in entropy measured in the case of these four metal complexes are quite expected as per the stability of complexes, and hence increase in entropy follow similar trend from Ni- to Hg-Complexes.

CONCLUSION

From the values of ΔS^0 obtained, it may be derived that the Standard Changes in Entropy goes on decreasing from Nickel to Mercury complexes. The values of ΔS^0 contribute much in stabilizing the Nickel complexes whereas it contributes less in the case of Cd- & Hg-complexes which belong respectively to 2nd and 3rd Transition metal series. Compared to these two, the value of ΔS^0 obtained in the case of Mn-complex contributes higher to the complex of Manganese which is a member of first transition metal series.

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