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Studies on Formation Constants of Some Bivalent Metal Complexes of Flurobenzoylthioacetone

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ABSTRACT

The Formation Constants of the complexes of p– fluorobenzoylthioacetone with some bivalent transition metals namely Iron, Cobalt, Cadmium and Mercury have been determined at three different temperatures potentiometrically using Calvin-Bjerrum potentiometric technique as modified by lrving and Rossotti. Para–fluorobenzoylthioacetone, an organic ligand is a bidentate chelating agent that forms a six-membered resonance stabilized chelate with bivalent transition metal ions. Both Stepwise and Overall formation constants of the complexes formed have been determined and discussed properly to know the stability order of the complexes synthesized.

Key−words: Formation Constant, Fluorobenzoylthioacetone, Potentiometric technique, Stability order.

INTRODUCTION

The ligand chosen for complexation with bivalent Iron, Cobalt, Cadmium and Mercury is para-fluorobenzoylthioacetone. This is a bidentata ligand which belongs to Monothio-β-Diketone class of compounds. It behaves as uninegatively charged bidentate chelating ligand after deprotonation through its enol or enethiol form giving a six-membered resonance stabilized ring complex with these metal ions.

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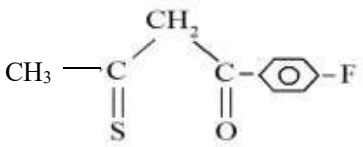

Fig.**1**: p- Fluorobenzoylthioacetone

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 to understand the effect of Fluorine substituent on the stability of metal complexes formed when compared with those of Benzoylthioacetone (the parent ligand) already reported.[1,2,3.]

In the present communication, we report the Overall Formation Constants of the complexes of p-fluorobenzoylthioacetone with Iron, Cobalt, Cadmium and Mercury at three different temperatures viz. 10°C, 20°C and 30°C at a fixed ionic strength of 0.1M KCl determined potentiometrically using Calvin-Bjerrum technique as modified by lrving and Rossotti. [5,6]

METHODOLOGY

By the reported method[4,7], the said ligand was synthesised by Claisen Condensation of o-ethylthioacetate with p-fluoroacetopheno-ne in presence of sodamide, and the crude product was recrystallized in ethanol, m.pt. 90°C (lit. 88-89°). The synthesis is shown below.

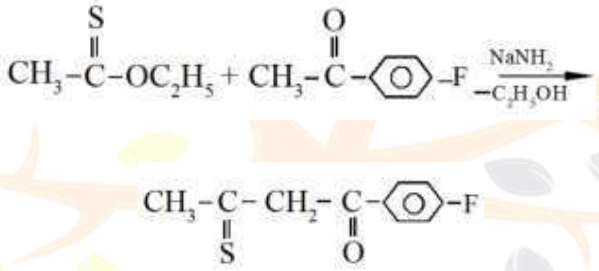

Fig.2 : p-Fluorobenzoylthioacetone

o-ethylthioacetate was prepared from acetonitrile by reacting it with ethanol, HCl and H_2S. Primary standard solution of ligand was prepared in dioxan[5]. Aqueous solutions of Metal (II) chlorides were standardized. KOH solution was prepared in CO_2-free conductivity water and was 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.

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 50ml so that volume of dioxan could remain 70% and the ionic strength as 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 was plotted in each case to get (i) Acid (ii) Ligand, and (iii) Complex Titration curves respectively[2,3,6.]

From acid and ligand titration curves, $\bar{n}_A$ values at various B-values were calculated through appropriate equation. A plot of $\bar{n}_A$ vs B gave the Formation Curve of Ligand–Proton complex. From this curve, pKa value of ligand (Protonation constant) was obtained by Half−Integral Method. The values of $\bar{n}$ and pL were calculated from Ligand and Complex titration curves using appropriate 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 Formation constants for each metal 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 are reported in Table-1 given below.

TABLE- 1

Stepwise and Overall Formation Constant Data of Complexes formed

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

Metal Ion	TEMPERATURE								
	10^0C			20^0C			30^0C		
	$LogK_1$	$LogK_2$	Logβ	$LogK_1$	$LogK_2$	Logβ	$LogK_1$	$LogK_2$	Logβ
Co^{++}	09.80	09.06	18.86	09.55	08.89	18.44	09.60	08.91	18.51
Fe^{++}	09.70	08.96	18.66	09.37	08.78	18.15	09.44	08.78	18.22
Cd^{++}	08.35	07.51	15.86	08.22	07.39	15.61	08.12	07.28	15.40
Hg^{++}	07.80	07.06	14.86	07.63	06.88	14.51	07.54	06.76	14.30

Thus, the Stability Order of Metal Complexes follow the trend :

Co (II) > Fe (II) > Cd (II) > Hg(II)

RESULTS & DISCUSSION

From the data obtained, it is obvious that the stability order of the complexes of metals in our present investigation with the ligand, p-fluorobenzoylthioacetone is : Co > Fe > Cd > Hg. The trend is found maintained at all the three temperatures namely 10°C, 20°C and 30°C. This can easily be found by studying the table down each temperature column. The overall formation constant values of all metal complexes with this ligand are higher at lower temperature than at the higher temperature with the only exception in the case of complexes of Cobalt and Iron at 30°C when compared their values at 20°C as is obvious form the above table. But here also $LogK_2$ values are lower than $LogK_1$ values as is found in the case of other complexes at all the temperatures.

The above trend is in conformity with the stability order reported for the complexes of these metals with other monothio-β-diketone ligands.[9,11] A comparison of the stability data of the present investigation with those of parent monothio-β-diketone complexes clearly reveals that the overall formation constant of all the four metal complexes are less than those of the respective complexes derived from Benzoylthioacetone, the parent ligand. This indicates that the substitution by Fluorine at para position of the Benzoyl ring in the ligand decreases the stability of the complexes formed which may be probably due to steric hindrance caused by Fluorine substituent. This may also be due to increased acidic strength of ligand as is obvious from its protonation constant value compound to its parent compound.

CONCLUSION

Though this sequence differs from the Mellor-Maley Series which has been found almost universally for oxygen and nitrogen donor ligands or Irving-willams Natural Order of stability, it is in conformity with the stability order reported for the chelates of these metals with several other monothio-β-diketones studied so far.[13,14] Also, while the ligand has a weak tendency to deprotonate, it has a strong tendency to coordinate the metal ions to form stable complexes. This is substantiated by low dissociation constant of the ligand and high stability constant of its complexes. All these complexes have numerous applications as pharmaceutical agents.

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DECLARATION

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

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