IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Studies on Enthalpy change during Complex Formation of Fluorobenzoylthioacetone with Fe, Co, Cd & Hg

[1]Sonal Kumari, [2]Manatosh Sadhu & [3]Hashmat Ali

1, 2. Research Scholar, PG Chemical Research Laboratory, S.K.M. University, Dumka, Jharkhand

3. Former Dean, Faculty of Science, S.K.M. University, Dumka, Jharkhand.

ABSTRACT

Complexes of p-Fluorobenzoylthioacetone with bivalent Iron, Cobalt, Cadmium and Mercury have many therapeutic uses. The Stability Constants of these complexes have been determined at three different temperatures namely 10°C, 20°C & 30°C using Calvin-Bjerrum potentiometric technique as modified by Irving and Rossotti. From a Knowledge of Overall Stability Constants, Standard change in Free energy were determined at the said temperatures using the appropriate Thermodynamic equation. The Standard changes in Enthalpy accompanying the complex formation reactions were determined with the help of Isobar equation as well as Gibbs-Helmholtz equation. These values of Enthalpy change which contribute towards complex formation have been propesly discussed.

Key-words: Fluorobenzoylthioacetone, Overall Stability Constant, Potentiometric Titration, Standard change in Enthalpy.

INTRODUCTION

The ligand chosen for complexation with bivalent Ferrum, Cobalt, Cadmium and Mercury is para-Fluorobenzoylthioacetone which belongs to Monothio-β-diketone class of compounds. It behaves as a uninegatively charged bidentate ligand after deprotonation through its enol or enethiol form in order to give six-membered chelates.[2,3,5] The structure of the ligand is shown below.

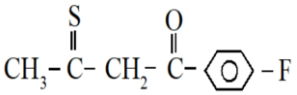

Fig1: p-Fluorobenzoylthioacetone

(The Ligand)

However, no attempt has been made so far to know the solution equilibria of this ligand and its derived chelates with said transition metals as also Standard change in Enthalpy accompanying the said chelations – a work that can help to know the contribution of Enthapy change towards said complex formation.[3,5,7]

In the present communication, we report the Stepwise and Overall Stability Constants of the complexes synthesized by the interaction of ligand chosen and four bivalent transition metal ions namely Iron, Cobalt, Cadmium and Mercury at 10°C, 20°C & 30°C, as also Standard change in Enthalpy accompanying the said complexation along with therapeutic uses of the complexes formed.

The Stability Constant of the complexes were determined by Calvin-Bjerrum's Potentiometric technique as modified by Irving and Rossotti[4,7,8.]

METHODOLOGY

The ligand chosen in the present investigation was synthesised by the interaction of o-Ethylthioacetate and p-Fluoroacetophenone in presence of sodamide through Claisen Condensation.[5,6] The crude product was recrystallized in ethanol, m.pt. 90°C (lit. 88-89°). The synthes is shown below.

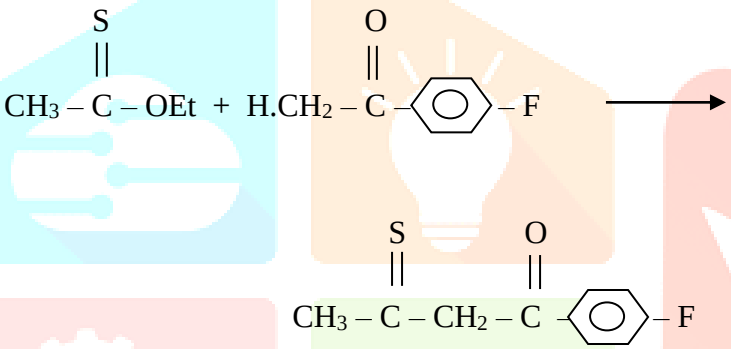

Fig.2 : Synthesis of p-Fluorobenzoylthioacetone

Primary standard solution of ligand was prepared in dioxan[8,9]. 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 solution was prepared in 1:1 dioxan-water medium to maintain the desired ionic strength. The temperatures were maintained constant at 10°C, 20°C and 30°C for three different experiments. A systronic pH-meter (accuracy ±0.01 pH unit) with combined glass and calomel electrodes was used for pH measurements.

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 50ml 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 was 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 HIM (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)]

$LogK_1^H = pKa$ =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
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

It is thus obvious from the above table, the stability order of above complexes follows the trend :

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

EVALUATION OF ΔG^0

The values of chage is Standard Free energy for these complexes at a particular temperature were evaluated by the thermodynamic expression, $\Delta G^0 = -2.303RT \log\beta$,

Where, β = overall stability constant, T = Temperature, R = constant

From a knowledge of overall stability constant data furnished in Table-1, the values of ΔG^0 at three different temperatures were evaluated for each metal complex, and are arranged below in Table-2.

TABLE- 2 :

ΔG^0 values of Metal Complexes at different tempts.

[μ= 0.1M KCl; Medium : 75% aq. dioxan]

Metal ion	$-\Delta G^0$ (in K Cals/mol)		
	Temperature		
	10 ^{0} C	20 ^{0} C	30 ^{0} C
Co^{++}	24.42	24.72	25.66
Fe^{++}	24.17	24.34	25.26
Cd^{++}	20.54	20.93	21.35
Hg^{++}	19.24	19.45	19.83

Thus, decrease in value of Standard change in free energy goes on increasing with increasing temperature.

DETERMINATION OF ΔH^0

The Standard change in Enthalpy (ΔH^0) associated with above complexation was determined by Linear Plot Method (Logβ vs 1/T) using following Isobar equation.[13,14,15]

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

The above equation may be rearranged as :

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

Taking R = 1.987 Cals. deg^{-1}. mol^{-1}, we have

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

According to this equation, the gradient of the tangent drawn at the point corresponding to any temperature on the curve obtained by plotting the values of log β as a function of 1/T will be equal to $-\frac{\Delta H^0}{4.576}$.

The result obtained is furnished below in Table-3.

TABLE-3.

ΔH^0 values of Bivalent Metal complexes obtained by LPM.

[μ= 0.1M KCl; Medium = 75% aq. dioxan]

Metal ions	$-\Delta H^0$ (K Cals/mol)
	By Linear Plot Method
Co^{++}	07.23
Fe^{++}	09.05
Cd^{++}	09.16
Hg^{++}	11.21

RESULTS & DISCUSSION

From the thermodynamic relation, $-\Delta G^0 = 2.303\ RT\ Log\beta$, it is obvious that β increases as ΔG^0 becomes negative, and as a result of it, a more stable complex is formed. In the present investigation, we find that like stability order (Table-1), the decrease in free energy change follows the same trend: Co (II) > Fe (II) > Cd (II) > Hg(II). Thus, the complexes formed are free energy stabilized.

So far as Standard change is Enthalpy is concerned, which has been determined by Linear Plot Method, shows a successive increasing value from Co-complex to Hg-complex. These values of standard change in Enthalpy are 07.23, 09.05, 09.16 and 11.21 K cals per mole respectively for the complexes of Cobalt, Iron, Cadmium and Mercury.

The negative value of Standard change in Enthalpy (ΔH^0) for each metal complex as given in Table-3 implies that the complex formation reactions are exothermic. Thus, all the metal complexes formed are Enthalpy stabilized.

CONCLUSION

From the data furnished in Table-3 which has been obtained by Linear Plot Method (Logβ vs 1/T), it is obvious that the Standard Change in Enthalpy (ΔH^0) conforming the stability order as listed in Table-I follows the same trend :

$$\mathbf{Co^{II} > Fe^{II} > Cd^{II} > Hg^{II}}$$

DECLARATION

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

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Kunul Kandir, Vice Chancellor, S.K.M. University, Dumka, Jharkhand.

REFERENCES

1. VOGEL A. I., 'A Text-Book of Practical Organic, Longmans, London, 3rd edition (1956).
2. Chaston S. & Livingstone S, Proceedings of the Chemical Society of London (Apr) III 1964.
3. Livingstone S. E., Coordination Chemistry Reviews, 7 (1), 59-80 (1971)
4. Joergensen, Brown, Carlsen & Duus, Journal of the American Chemical Society, 104 (22), 5922 (1982)
5. Calvin. M & Wilson. K, Journal of the American Chemical Society, 67 (II), 2003 (1945)
6. Bjerrum J., Metal amine Formation in aqueous solution, Haase, Copenhagen (1941)
7. M. Cox & J. Darken, Coord. Chem. Review, 7, 29 (1971)
8. H. M. Irving & H. S. Rossotti, J. Chem. Soc. 2904 (1954)
9. Choudhary & Ali, J. Indian Chemicel Society, 68, 257 (1991)
10. Ali, Kumar & Kumar, J. Chemtracks, A division of American Chemical Society, Vol. 18, No.1, pp. 205 - 210 (2016)
11. Hashmat Ali et al, International Journal of Creative Research Thoughts, IJCRT2205706, Vol. 10, issue 5, pp - 109-121 (2022)
12. Ali, Kumar & Soren, International Journal of Current Science, IJCSPUB, Vol. 12, issue 2, pp. 693 -704 (2022)
13. Ali & Panda, International Journal of Chemical and Physical Sciences, IJCPS Vol. 7, No. 3, pp. 81-87 (2018)
14. Hashmat Ali et al, The Scientific Temper, A Web of Science Journal, Vol. 13, No.2, pp. 160-164 (2022)
15. Kumar, Soren & Ali, Biospectra , An international Biannual Refreed Journal of life Sciences, Vol. 17 (2), pp. 179-182 (2022)
16. Sahay & Ali, International Journal of Creative Research Thoughts, IJCRT2507714, Vol. 13, Issue 7, pp. 742-746 (2025)