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Evaluation of Change in Entropy during Complexation of Fluorobenzoylthioacetone with Some Bivalent Metal ions with their Medicinal Significance.

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ABSTRACT

The Stability Constants of the complexes of Fluoro substituted benzoylthioacetone with bivalent Transition metals namely Iron, Cobalt, Cadmium and Mercury at three different temperatures viz. 10°C, 20°C and 30°C have been determined potentiometrically. With good entropy change values, these complexes have good therapeutic importance. From a knowledge of Overall Stability Constants of the complexes formed, Standard changes in Free energy, Enthalpy and Entropy associated with the said complex formation were determined using the appropriate thermodynamic equation. From the data obtained, Standard change in Entropy accompanying the said complexation together with their medicinal significance have been discussed.

Key-words: Formation Constant, p-fluorobenzoylthioacetone, Potentiometric technique, Entropy.

INTRODUCTION

Para-fluorobenzoylthioacetone, the ligand of present research work is an organic ligand belonging to Monothio-β-diketone class of compounds. Complexation of this ligand were made with bivalent Fe, Co, Cd and Hg. The ligand behaves as a uninegatively charged bidentate chelating agent after deprotonation through its enol or enethiol form giving six-membered resonance stabilized ring with these metal ions. The structure of the ligand is shown below.

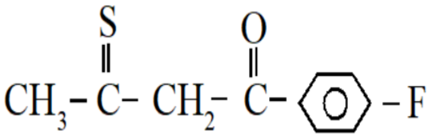

Fig.1: para-fluorobenzoylthioacetone

(The Ligand)

However, no attempt has been made so far to study the solution equilibria of this ligand and its derived complexes with metal ions taken as also standard changes in Entropy of the above complexes and their medicinal values – a work that can help us to know the chelating ability of the ligand and change in Entropy associated with formation of these complex together with their medicinal importance.

In the present communication, we report the Overall Stability Constants of the complexes of p-fluorobenzoylthioacetone with Fe, Co, Cd and Hg at three different temperatures at a fixed ionic strength of 0.1 M KCl by Calvin-Bjerrum potentiometric technique as modified by Irring and Rossotti. Besides, the Standerd Change in Entropy associated with above complexation has been determined using appropriate thermodynamic expression. Also, the medicinal values of these complexes have been described.

EXPERIMENTAL

The ligand was synthesised by the reaction of o-ethylthioacetate

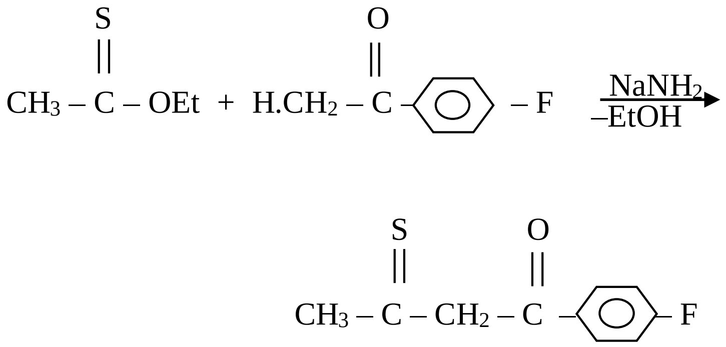

Fig.2 : Synthesis of p-Fluorobenzoylthioacetone

with 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.

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 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**
Co^{II}	09.80	09.06	18.86	09.55	08.89	18.44	09.60	08.91	18.51
Fe^{II}	09.70	08.96	18.66	09.37	08.78	18.15	09.44	08.78	18.22
Cd^{II}	08.35	07.51	15.86	08.22	07.39	15.61	08.12	07.28	15.40
Hg^{II}	07.80	07.06	14.86	07.63	06.88	14.51	07.54	06.76	14.30

From Table-I, it is clear that the Stability order of the complexes formed follows the trend : **$Co^{II} > Fe^{II} > Cd^{II} > Hg^{II}$**

The value of Standard Chage in Free energy was evaluated through thermodynamic expression, $\Delta G^0 = -2.303RT \log\beta$,

Where, β = overall stability constant, T = Temperature, R = constant. The values of ΔG^0 obtained at different temperatures for each metal complex are furnished 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)**		
	10 ^{0} C	**20 ^{0} C**	**30 ^{0} C**
Co^{II}	24.42	24.72	25.66
Fe^{II}	24.17	24.34	25.26
Cd^{II}	20.54	20.93	21.35
Hg^{II}	19.24	19.45	19.83

Thus, from the table it is obvious that the decrease in Standard free energy is higher at higher temperature in the case of each metal complex.

The standard vhange in Enthalpy accompanying the above complex formation was determined by Isobar equation. These values of ΔH^0 obtainable form the plot of Logβ Vs 1/T (Linear Plot Method) are listed 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^{II}	07.23
Fe^{II}	09.05
Cd^{II}	09.16
Hg^{II}	11.21

Thus, there is a successive increase in the value of standard change in Enthalpy from Co-complex to Hg-complex (Table-3).

EVALUATION OF **ΔS^0** (Standard Change in Entropy)

The values of Standard Change in Entropy were calculated using values of **ΔH^0** obtained by Linear Plot Method (Logβ vs 1/T). These values of **ΔS^0** were calculated through the Thermodynamic equation, **$\Delta G^0 = \Delta H^0 - T\Delta S^0$**. The required values of **ΔG^0** and **ΔH^0** are mentioned respectively in Table-2 and Table-3. The values of **ΔS^0** are furnished below in Table-4.

TABLE-4.

ΔS^0 values of Bivalent Metal complexes

Metal ions	$-\Delta S^0$ (K Cals/mol)
Co^{II}	59.69
Fe^{II}	52.18
Cd^{II}	40.17
Hg^{II}	28.12

Thus, the Standard Change in Entropy follows the same trend.

RESULTS & DISCUSSION

From the thermodynamic relation, $-2.303\ RT\ \mathrm{Log}\beta = \Delta G^0 = \Delta H^0 - T\Delta S^0$, it is obvious that β increases as ΔG^0 becomes more negative. Thus, 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. In the present investigation, we find that all the thermodynamic parameters viz. ΔG^0, ΔH^0, and ΔS^0 in conformity with the stability order of the complexes 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 for these complexes, it is clear that Cobalt complex is much entropy stabilized having maximum disorderness. Thus, the values of ΔS^0 obtained support the stability order : **Co (II) > Fe (II) > Cd (II) > Hg(II).**

From table-4, we find that the values of Standard Change in Entropy in the case of complexes of cobalt, Iron, cadmium and Mercury are 59.69, 52.18, 40.17 and 28.12 K

Cals/mol respectively when determined using values of ΔH^0 obtainable by Linear Plot Method. It is noticeable that the increase in entropy measured in the case of the above four complexes synthesized are quite expected as per the stability order of complexes, and hence increase in entropy follows the same trend from Cobalt-complex to Mercury-complex.

Coordination compounds have great significance in biological system because of having specific structural arrangements. These complexes have been found much curative as antibacterial drugs.

CONCLUSION

From the results obtained, it may be concluded that the Standard Changes in Entropy furnished in Table-4 clearly support the Stability Order of the complexes formed. Complex compounds play vital role in biological system. These complexes of p-fluorobenzoylthioacetone have been found antibacterial. The values of ΔS^0 obtained clearly suggest that the complexes formed are considerably stable and therefore have good therapeutic values. These complexes show effective behaviour in Malaria also.

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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