IJCRT.ORG ISSN : 2320-2882
INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

Analysis Of Equilibrium and Thermodynamics Parameter of Metal Chelates Tb (III) and Th (IV) p-Chlorobenzaldehydethiosemicarbazone Systems

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Abstract:

Co-ordinate compounds shows their importance in nature , hemoglobin, chlorophyll and vitamin B_{12} are few examples ,coordinate compounds also shows utility in dye and pigments .Fertilizer and pesticides are also available in complex compound form it shows better absorption by plants[10]. Co-ordination compounds are widely showing their use in medicine and drugs field. Coordinate compound of few metals with Schiff's base ligands shows antibacterial [1-3] and some complexes also shows anti- carcinogenic properties such as co-ordinate compound of Tb (III) and Th (IV)- p-chlorobenzaldehydethisoemicarbazone[17]-[19] , to understand its action and its reaction mechanics it is important to know its structure and its stability in solution. Presently studies are focused on stability of complex, Tb(III) and Th(IV)- p-chlorobenzaldehydethisoemicarbazone) with the help of stability constants of each steps when co-ordination number is one, two, three (Tb and Th) and four (Th) with the help of formation constants , Equilibrium analysis also carried out by using pH of legend solution and by adding metal ion solution calculation is done by using Bjerrum equation[4] and also by graphical method., and Bjerrum equation is applied. Thermodynamics parameters also determine such as standard enthalpy of reaction, standard entropy and standard free energy of the system to understand feasibility of the process.

Key words: Co-ordinate compound, entropy, free energy, stability constant

Introduction:

Schiff's ligands thiosemicarbazones exhibit of tautomerism in solution, due to conjugate structure (-N = N-C=O), in solution it exist as a thioketo-thioenol form due to its enolic structure it behave as a bi-dentate legends hence form very stable chelates with metals . Existence of thioketo – thioenol system in them has been based by Sawhney and Coworker consequent to IR and NMR information [13]-[16]. Equilibrium analysis of Tb (III) -, and Th (IV) – p-chlorobenzaldehydethisoemicarbazone systems by taking up their pH studies, is here presented. The study here revolves around the functions : protonation constant (PK_H) of p-chlorobenzaldehydethiosemicarbazone the stability constant (k_1, k_2, k_3 and k_4) and thermodynamic functions enthalpy of formation (ΔH), entropy of formation (ΔS) and free energy change (ΔG)of metal p-chlorobenzaldehydethiosemicarbazone systems.

Extent of metal interaction to p-chlorobenzaldehydethiosemicarbazone (ligand number, $\bar{n}$) has been calculated following Bjerrum's concept [4] on metal ligand interaction in solution.

Another function pL (free ligand exponent) which has a role to play for the cause under study has been worked out from the relationship given by Bjerrum equns.(1-1, 1-2).

$L = \frac{\Delta NaOH}{(1+ H^+/K)}$ 1-1

$pL = \frac{1+10^{-pH}.pK_H}{\Delta NaoH}$ 1-2

Following eqn. (1-3) the graphical approach

$\log K_n = pL + \log \bar{n}-(n-1) /n- \bar{n}$ 1-3

Using equ.(1-3) $\log K_1$, $\log K_2$ and $\log K_3$ values can be determine (Table 1 and 2)

pK_H - Protonation constant, $\bar{n}$- ligand number, pl- Free ligand exponent, β -overall stability constant of metal complex having 1 : 3 for Tb - p-chlorobenzaldehydethiosemicarbazone and 1:4 for Th -p-chlorobenzaldehydethiosemicarbazone composition.

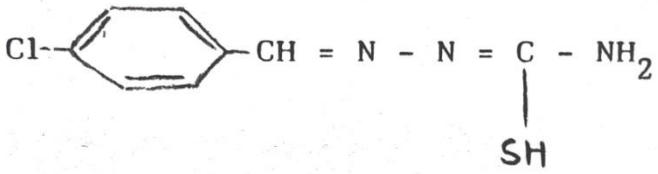
Reagents: Analytical grade. chemicals were used

HNO_3 : 0.1 M (aq)
KNO_3 : 1 M (aq)
NaOH : 0.1 M (aq)
p-chlorobenzaldehydethiosemicarbazone : 0.01 M (in acetone)
Metal nitrates: 0.01 M Tb (III) and 0.01 M Th (IV) Acetone

pH Studies
pH metric titrations of each of the following set (50 ml) ,
1 : 5ml M KNO_3, 2ml 0.1 M HNO_3, 18ml water, 25ml acetone.
2 : 5ml M KNO_3, 2m, 0.1 M HNO_3, 18ml water, 5ml 0.01 M ligand, 20ml acetone.
3 : 5ml M KNO_3 , 2ml 0.1 HNO_3, 5ml 0.01 M ligand , 1ml 0.01 M metal ion, 17ml water, 20ml acetone
is titrated using 0.1 M NaOH solution. It was performed on a Beckman pH-meter H-2 with. The pH values were corrected for volume and nonaqueous medium as suggested by van uitert and Hass[12].

RESULTS AND DISCUSSION

p-Chlorobenzaldehydethiosemicarbazone, which tautomerism in solution generating thioketo – thioenol system, is a monoprotic acid, as explained earlier by Sawhney and Coworkers [13]-[16],



Thioenol form
(p-chlorobenzaldehydethiosumicarbazone)

with –SH as a salt forming group, as a result of which the pH-metric investigation on the extent of interaction of this chelator to some of the elements: Tb (III), (4f block elements) and Th (IV) (5f block element) in non-aqueous medium (50% acetone in water by volume) could be made possible.
The whole study was carried out infinite dilution and at constant ionic strength. Under the applied condition, the situation probably ruled out the formation of polynuclear species in solution. Secondly the study could be said to be carried out in thermodynamically true environment and the equilibrium constants under these applied conditions turned out to be thermodynamic formation constants. Information on the combining ratio of species formed in solution could be gathered from the values of $\bar{n}$ (degree of formation). In Tb (III) p-chlorobenzaldehydethiosemicarbazone systems, $\bar{n}$ approximated to three while its values for

Th (IV) p-chlorobenzaldehydethiosemicarbazone system turned out to be four: the four former systems produced species having 1:1, 1:2 and 1:3 composition whereas the latter one pointed to the existence of 1:1, 1:2, 1:3 and 1:4 species in solution.

In solution formation constants of each step could be determine using values of degree of formation($\bar{n}$). in Bjerrum equation[4]. The data on diverse metal-p-chlorobenzaldehydethiosemicarbozone systems revealed the adherence to the basic conditions necessary for its justification, that is, log $k_1/k_2 \geq 2.5$ Another approach followed in the estimation of stepwise formation constants was of graphical one. Comparison of data derived from both methods manifested an agreement (Tables - 1 and 2).

Earlier reported values of protonation constants of p-chlorobenzaldehydethiosemicarbazone at 28^0 C (log PK_H = 10.25) and 38^0 C (log PK_H = 9.70) have been employed here to work out metal-ligand stability constants of the above systems. To prevent metal hydrolysis each set had been prepared as to have 1:5 ratio of metal to ligand.

The stability data on the systems (28^0C/38^0C) studied evinced the highest bond strength when metal ion interacts with one molecule of the ligand(1:1), and which decreased with the successive increase of coordination number . log K_1 > log K_2 > log K_3 > log K_4(Table 1and 2) in solution. On screening the data further constants (K_1, K_2, K_3, K_4) Tb (III) and Th (IV) p-chlorobenzaldehydethiosemicarbazone systems was observed indicating low temperature to be favourable for metal-ligand interaction in solution and which in turn suggested the lowering of stability of the system and which in turn suggested the lowering of stability of the system, this is, decrease in constants values with rise of temperature attributable to the decrease in kinetic energy of molecules involved.(In Tables : 1 and 2) are given the data due to graphical method. pH-titration data on different systems are displayed in, The reactions [Tb (III) -, Th(IV)- p-chlorobenzaldehydethiosemicarbazone are exothermic (- ΔH^0), The free energy change with negative sign (- ΔG^0) indicated thermodynamic feasibility of the reactions. This decreased with the higher temperature. It suggests exothermic reactions, were less feasible at higher temperature. The reactions between Tb ion and Th ion with legends, the present results in suggest and conclusions drawn on the participation of the terminal hydrazine nitrogen N(III) atoms by Goronbak et.al.[5], Beecroft et.al.[6], Ronoldhaines et.al[7]. and Malik et.al.[8] through spectroscopic studies, could lead to the following structures.

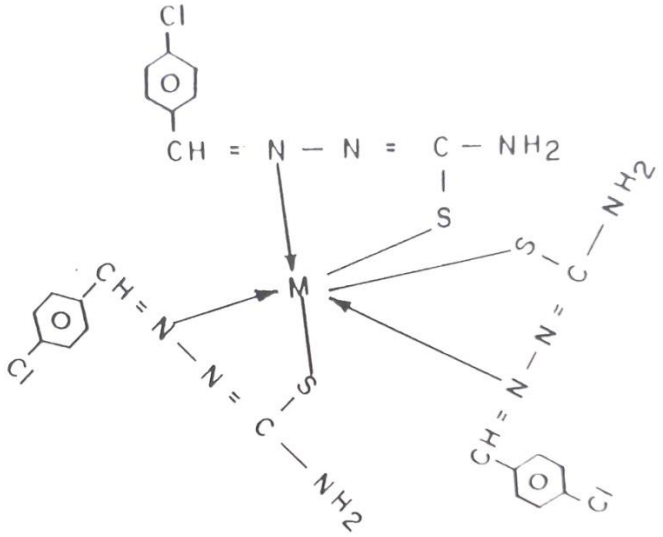


Fig 1, M= Tb(III)

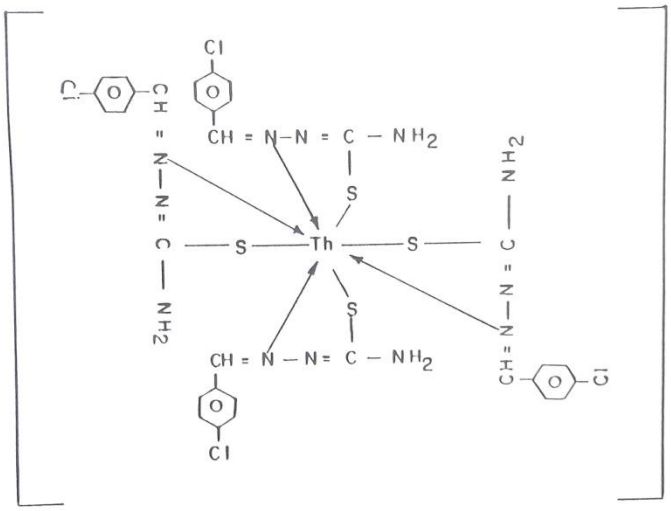


Fig-2

Table 2

Stability and Thermodynamic Data for Tb (III)-p-chlorobenzaldehyde-thiosemiccarbazone system.

Parameter	Methods	Temperature (°C)	
		28^0	38^0
log k_1	A	9.95	8.65
	B	8.95	8.60
log k_2	A	5.65	5.45
	B	5.40	5.75
log k_1 / k_2	A	3.90	3.20
log k_3	A	5.00	5.00
	B	5.00	5.00
log β	A	20.20	19.10
	B	19.35	19.35
Mean		21.13	21.13
ΔG^0(kcal mol^{-1},		-27.24	-27.35
ΔH^0(kcal mol^{-1})		-27.84	-27.84
ΔS^0(cal mol^{-1} deg^{-1})			-177.00

Method : A – Bjerrum technique, B = graphical method

Table 2

Stability and Thermodynamic Data for Th(III)-p-chlorobenzaldehyde-thiosemiccarbazone system.

Parameter	Methods	Temperature (°C)	
		28^0	38^0
log k_1	A	8.95	8.60
	B	8.90	9.60
log k_2	A	6.75	5.65
	B	6.70	6.95
log k_1 / k_2	A	2.20	2.95
log k_3	A	5.33	5.00
	B	5.3	5.00
log k_4	A	5.00	5.00
	B	5.00	5.00
log β	A	26.03	24.25
	B	25.95	26.90
Mean		25.99	25.4
ΔG^0(kcal mol^{-1}),		-35.80	-31.15
ΔH^0(kcal mol^{-1})		-25.27	-25.27
ΔS^0(cal mol^{-1} deg^{-1})			-197.00

Method: A – Bjerrum technique, B = graphical method

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