

## EQUILIBRIUM AND STABILITY ANALYSIS OF METAL CHELATES OF ND AND PR METALS WITH P CHLOROBENZALDEHYDETHIOSEMICARBAZONE SYSTEM

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### ABSTRACT

Co-ordination compounds now days deserving attention due to their wide use in bio-chemistry, analytical chemistry and in agriculture industries(8), co-ordination compounds of thiosemicarbazone (ligand) with Nd, Pr, Gd, Eu etc shows their use as an anticancer properties(1-3) so it required more attention. In order to understand nature of bonding between metals and the ligand in solution and to determine the stability in solution study is essential and important. In present study varies parameters which are useful are calculated by using change in pH of ligand and its metal complex at 28°C and 38°C, Formation constants, free energy change, entropy change and heat of reactions also calculate to determine the feasibility of complex formation.

**KEYWORDS:** pH, free energy, entropy, stability constant.

### INTRODUCTION

Thiosemicarbazones exhibit tautomerism in solution, due to having conjugation (-N=N-C=O) system so it exist in dynamic equilibrium in thioketo-thioenol form so these ligand form chelates with metals. Existence of thioketo – thioenol system in them has been based by Sawhney and Coworker consequent to IR and NMR information.<sup>[4-7]</sup>

Equilibrium analysis of Nd (III) -, Pr (III)- p-chlorobenzaldehydethiosemicarbazone systems by taking up their pH studies, is here presented.

### MATERIAL AND METHODS

Chemicals used were of analytical grade.

#### Reagents

1. HNO<sub>3</sub>: 1 x 10<sup>-1</sup> M (aq)
2. KNO<sub>3</sub>: 1 x 10<sup>0</sup> M (aq)
3. NaOH: 1 x 10<sup>-1</sup> M (aq)
4. Thiosemicarbazide:
5. p-chlorobenzaldehyde:
6. p-chlorobenzaldehydethiosemicarbazone: 0.01 M (in acetone)
7. Metal nitrates: 0.01 M (Metals: Nd (III) and Pr (III)) Acetone:

#### pH Studies

pH titrations of each of the following set, 50 ml of which had

I: 2ml 0.1 M HNO<sub>3</sub>, 5ml M KNO<sub>3</sub>, 18ml water, 25ml acetone.

II: 2ml, 0.1 M HNO<sub>3</sub>, 5ml M KNO<sub>3</sub>, 18ml water, 5ml 0.01 M ligand, 20ml acetone.

III: 2ml 0.1 HNO<sub>3</sub>, 5ml M KNO<sub>3</sub>, 17ml water, 5ml 0.01 M ligand, 1ml 0.01 M metal ion, 20ml acetone

Were performed on a Beckman pH-meter H-2 with 0.1 M NaOH. The pH values were corrected for volume and non-aqueous medium as suggested by van uitert and Hass(16).

#### Expression Involved

The study here revolves around the functions: protonation constant of p-chlorobenzaldehydethiosemicarbazone, the stability constant and thermodynamic functions of metal – p-chlorobenzaldehydethiosemicarbazone systems.

Extent of metal interaction to p-chlorobenzaldehydethiosemicarbazone (ligand number,  $\bar{n}$ ) has been gauged following Bjerrum's concept (8) 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 (eqns. 1-1, 1-2).

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

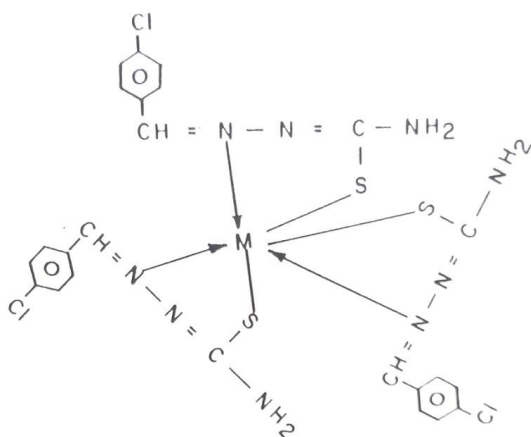
$$\text{or } pL = \log \frac{1 + 10^{-pH} \cdot P_k H}{\Delta \text{NaOH}} \quad 1-2$$

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

Equation 1-3, is for graphical method using this equation formation constants of each steps ( $k_1$ ,  $k_2$ ,  $k_3$ ) of the system can be determine

#### Nomenclature

1.  $pK_H$ : Protonation constant
2.  $\bar{n}$ : ligand number
3.  $pL$ : Free ligand exponent
4.  $\beta$ : overall stability constant of metal complex having 1 : 3 composition.



(Fig 1), M= Pr(III) and Nd(III)

**Table 1: Stability of formation and Thermodynamic Data for Pr(III)-p-chlorobenzaldehydethiosemicarbazone system.**

Parameter	Method*	Temperature (°C)	
		28 <sup>0</sup>	38 <sup>0</sup>
log $k_1$	I	7.80	8.90
	II	8.45	8.90
log $k_2$	I	6.05	6.15
	II	6.15	6.20
log $k_1 / k_2$	I	1.75	2.75
log $k_3$	I	5.05	5.10
	II	5.00	5.05
log $\beta$	I	18.90	20.15
	II	19.60	20.15
Mean		19.25	20.15
$\Delta G^0$ (cal mol <sup>-1</sup> )		-26795	-28615
$\Delta H^0$ (cal mol <sup>-1</sup> )		+21425	+21425
$\Delta S^0$ (cal mol <sup>-1</sup> )			+163

\* I – Bjerrum technique, II = graphical method

**Table 2: Stability of formation and Thermodynamic Data for Nd(III)-p-chlorobenzaldehydethiosemicarbazone system.**

Parameter	Method*	Temperature (°C)	
		28 <sup>0</sup>	38 <sup>0</sup>
log $k_1$	I	8.20	8.35
	II	8.20	8.25
log $k_2$	I	5.80	6.30
	II	5.05	5.70
log $k_1 / k_2$	I	2.45	2.05
log $k_3$	I	5.05	5.25
	II	5.05	5.25
log $\beta$	I	19.05	19.90
	II	18.30	19.20
Mean		18.65	19.55
$\Delta G^0$ (cal mol <sup>-1</sup> )		-25985	-28125
$\Delta H^0$ (cal mol <sup>-1</sup> )		+25974	+25464
$\Delta S^0$ (cal mol <sup>-1</sup> )			+176

\* I – Bjerrum technique, II = graphical method

#### RESULTS AND DISCUSSION

p-Chlorobenzaldehydethiosemicarbazone, which tautomerises in solution generating thioketo – thioenol system, is a monoprotic acid, as explained earlier by Sawhney and Coworkers,

Information on the combining ratio of species formed in solution could be gathered from the values of  $\bar{n}$  (degree of formation). In Nd(III) and Pr(III)- p-chlorobenzaldehydethiosemicarbazone systems,  $\bar{n}$  approximated to three produced species stepwise having 1:1, 1:2 and 1:3 composition species in solution.

To calculate the values of formation constants of each steps of complex formation when the co-ordination number is one two and three:  $k_1$ ,  $k_2$ ,  $k_3$  or  $k_4$ , respectively Bjerrum & technique is used.

The stability constants data of complex formation suggest (28<sup>0</sup>/38<sup>0</sup>C) the highest bond strength when metal ion interacts with one molecule of the ligand, and stability constant decreased with the successive attachment of ligand molecules ( $\log K_3 < \log K_2 < \log K_1$ ) in solution. On screening the data formation constants ( $K_1$ ,  $K_2$ ,  $K_3$ ) of Pr(III) -, Nd(III) p-chlorobenzaldehydethiosemicarbazone systems the rise of constants values with the rise of temperature due to

increase of kinetic energy of the molecules which participating in the reactions.

The reactions [Pr (III) -, Nd(III) with p-chlorobenzaldehydethiosemicarboazone are endothermic in nature ( $+\Delta H^0$ ). The free energy change are negative sign ( $-\Delta G^0$ ) (Pr(III), Nd(III), p-chlorobenzaldehydethiosemicarboazone system) indicated thermodynamic feasibility of the reactions. At higher temperature the more negative  $\Delta G^0$  values which suggest reaction is more favourable at higher temperature. Further negative  $\Delta G^0$  values suggest the spontaneous nature of the reactions. Positive  $\Delta S^0$  further suggest complex formation is favourable. The present results in combination with the conclusions drawn on the participation of the terminal hydrazine nitrogen N(III) atoms by Goronbak et.al.(9), Beecroft et.al.(10), Ronoldhaines et.al.(11) and Malik et.al.(12). through spectroscopic studies, could lead to the following structures.

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