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Evaluation of Standard Changes in Free Energy During Complexation of p-chlorobenzoylthioacetophenone with Some Bivalent Transition Metals

Hashmat Ali, Nishant Soren*, Rohit Kumar Ravi, Kunal Kumar and Anjali
University Department of Chemistry, Sido Kanhu Murmu University, Dumka-814110, Jharkhand, India
**Corresponding author: nishantsoren3@gmail.com*

ABSTRACT

Para-chlorobenzoylthioacetophenone is an organic ligand of monothio-β-diketone class. Stability constants of bivalent complexes of manganese, nickel, palladium and platinum at three different temperatures were determined using Calvin-Bjerrum's pH-metric technique as adopted by Irving and Rossotti. From the data of stability constant of the complexes obtained, standard changes in free energy at the said temperatures namely 283K, 293K and 303K were determined with the help of thermodynamic relation, $\Delta G° = -2.303\ RT\ \text{Log}\ \beta$. Standard changes in free energy contributing towards complex formation have been discussed.

Keywords: Free energy, p-chlorobenzoylthioacetophenone, Potentiometric Titration, Stability Constant, Solution equilibria

INTRODUCTION

The ligand, p-chlorobenzoylthioacetophenone is considered for complexation with bivalent manganese, nickel, palladium and platinum. This ligand belongs to monothio-β-diketone[1,2,3] class of compounds.

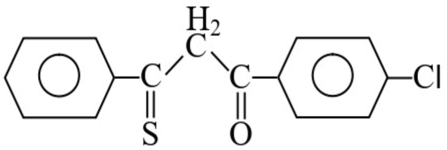

Figure 1: p-chlorobenzoylthioacetophenone

The said ligand acts as a bidentate chelating agent after deprotonation through its enol or enethiol[4,5,6] form forming a six-membered resonance stabilized chelate[7] with mainly transition metal ions.

No effort has been made till now to study the solution equilibria of this ligand and its derived metal complexes as well the standard changes in free energy accompanying the complex formation – a work which can facilitate in understanding the contribution of ΔG° (standard change in associated free energy) towards said complexations.

Through this communication, we present the stepwise and overall stability constants[8,9,10] of the metal complexes of manganese, nickel, palladium and platinum (all bivalent) with said ligand at three different temperatures namely 283K, 293K and 303K at a fixed ionic strength of 0.1 M potassium chloride. Stepwise and overall stability constants of the complexes were determined by Calvin-Bjerrum's[11,12] potentiometric titration method as employed by Irving and Rossotti[13]. We also report the changes taking place in thermodynamic factor viz. free energy accompanying the complexations.

MATERIALS AND METHODS

The ligand, p-chlorobenzoylthioacetophenone was synthesised by the Claisen condensation reaction of o-ethylthiobenzoate with p-chloroacetophenone in the presence of sodamide. The ligand solution was prepared in dioxan[14,15].

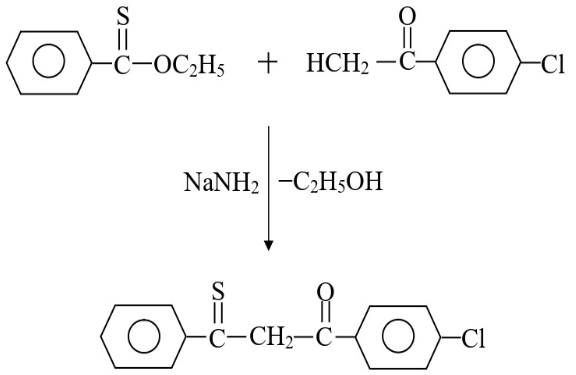

Figure 2: Synthesis of p-chlorobenzoylthioacetophenone

Following three sets of solutions were prepared:

i) 5 ml 0.4 M HCl solution + 5 ml M potassium chloride solution

ii) Mixture (i) + 5 ml 0.02 M solution of ligand

iii) Mixture (ii) + 5ml 0.004 M solution metal ion

The volume in each set was kept 50 ml in such a manner that dioxan volume remained 70% and ionic strength was maintained at 0.1 M KCl. The mixtures were titrated against 0.2 M potassium hydroxide solution. Oxygen-free nitrogen atmosphere was maintained for the pH measurement. A graph was plotted between pH-meter readings and the volume of alkali in each case was designated as acid, ligand and complex titration curves respectively.

Values at different pH-meter readings (B-values) were determined from acid and ligand titration curves using appropriate equation. A graph of versus B provides the formation curve of the ligand-proton complex. The pKa value of ligand (K_1^H = 1/Ka) was obtained by half integral method[12,16] (HIM) from the formation curve obtained. Thus, Log K_1^H = pKa = B at $\bar{n}_A$ = 0.5. Here, pKa is protonation constant.

This was again validated by linear plot of Log $\bar{n}_A/\left(1-\bar{n}_A\right)$ versus B. The values of versus pL were evaluated from the ligand and complex titration curves using appropriate equations. A graph of $\bar{n}$ versus pL gave the formation curves of the metal-ligand complexes. The stepwise stability constants of each complex (Log K_1 and Log K_2) were determined by half integral method (HIM). Thus, we get Log $K_1 = pL$ at $\bar{n}$ = 0.5 and Log $K_2 = pL$ at $\bar{n}$ = 1.5. The difference between the values of Log K_1 and Log K_2 was notably small. Therefore, it was refined by least square treatment[16] (LST).

On the basis of experimental data, following graphs were obtained.

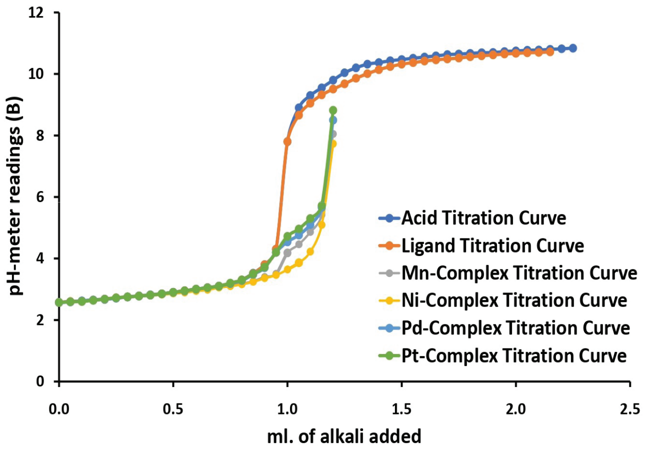

Figure 3: Acid, Ligand and Metal-Complex Titration Curve at 283K

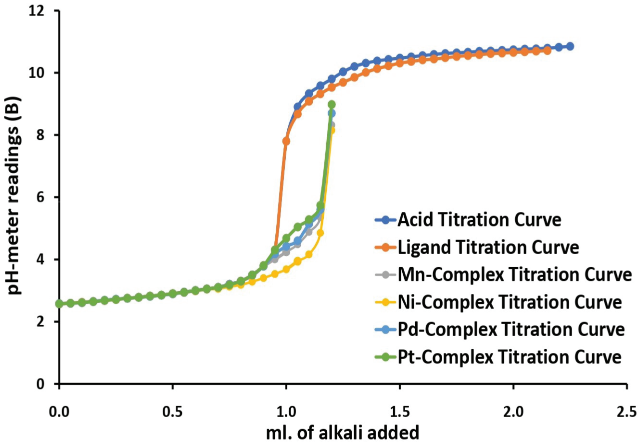

Figure 4: Acid, Ligand and Metal-Complex Titration Curve at 293K

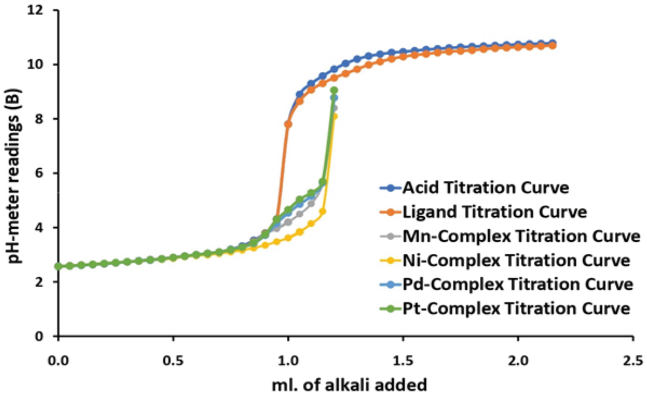

Figure 5: Acid, Ligand and Metal-Complex Titration Curve at 303K

RESULTS AND DISCUSSION

From the experiments performed, the data related to stepwise and overall stability constant of the complexes are furnished below in Table-1.

Table-1: Stepwise and Overall Stability Constant Data of Metal Complexes at 283K, 293K and 303K

Metal Ions	Temperatures								
	283K			293K			303K		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Ni^{2+}	10.59	09.75	20.34	10.37	09.48	19.85	10.31	09.45	19.76
Mn^{2+}	09.48	08.79	18.27	09.32	08.69	18.01	09.24	08.55	17.79
Pd^{2+}	09.11	08.51	17.62	09.12	08.39	17.51	08.83	08.29	17.12
Pt^{2+}	08.93	08.39	17.32	08.77	08.23	17.00	08.63	08.14	16.77

As is evident from the above table, the stability constant of metal complexes follow the order: $Ni^{II} > Mn^{II} > Pd^{II} > Pt^{II}$

The standard change in free energy[17,18] at a particular temperature has been determined by employing the thermodynamic expression given below.

$-\Delta G° = 2.303\ RT\ \text{Log}\ \beta$

Where, ΔG° = Standard change in free energy associated with the complex formation reaction

R = constant

T = temperature in kelvin

β = overall stability constant

Table-2 :Standard free energy change of metal complexes at 283K, 293K and 303K

Metal ions	$-\Delta G°(\text{kcal mol}^{-1})$		
	Temperatures		
	283K	293K	303K
Ni^{2+}	26.34	26.61	27.40
Mn^{2+}	23.66	24.15	24.67
Pd^{2+}	22.82	23.48	23.74
Pt^{2+}	22.43	22.79	23.25

Thus, the decrease in standard free energy change values are lower at 283K than at 293K which in turn are lower than those at 303K for the complexes of each metal. From the thermodynamic relationship viz. $-RT \ln \beta = \Delta G°$, it follows that the overall stability constant increases as standard free energy change becomes more negative. This results in the formation of more stable metal complexes. Moreover, greater the amount of heat liberated, more stable will be the product of a reaction.

In the present investigation, we come to know that free energy change values also in conformity with the stability order as listed in Table-1 follow the same order. $Ni^{II} > Mn^{II} > Pd^{II} > Pt^{II}$

Thus, the metal complexes formed are free energy stabilized. This supports the order of stability observed in the case of complexes of all the four bivalent metal ions.

CONCLUSION

The highest decrease in standard free energy change at each temperature is possessed by the complexes of nickel whereas lowest value is displayed by the complexes of platinum. Thus, at 303K, free energy change value is equal to 27.40 kcal mol^{-1} for Ni-complex whereas it is just 23.25 kcal mol^{-1} in the case of complex of platinum.

It is imperative to know here that platinum belongs to third transition elements series which has comparatively less tendency to form stable complexes compared to the metals of first transition elements series. This is obvious when we look at the table where we can find that higher values of decrease in standard free energy is possessed by the members of first transition elements series namely nickel and manganese.

Thus, supporting the stability order (overall stability constant values of the complexes as mentioned in Table-1), the decrease in standard change in free energy at each temperature follow the same order: $Ni^{II} > Mn^{II} > Pd^{II} > Pt^{II}$

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Declaration: *We also declare that all ethical guidelines have been followed during this work and there is no conflict of interest among authors.*

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