

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES THERMODYNAMIC STUDIES OF TRANSITION METAL COMPLEXES WITH HYDROXY SUBSTITUTED CHALCONE IN MIXED SOLVENT SYSTEM PH METRICALLY

Mohd. Wajid W. Shaikh^{*1} & S.D.Thakur²

^{*1}Research Student, ²Assistant Professor, Department of Chemistry, Bar. R.D.I.K & N.K.D Science College, Badnera (M.S), India

Abstract

In the present work we investigate the stability constant of 1-(5-bromo-2-hydroxyphenyl)-3-(2-chlorophenyl) prop-2-en-1-one [BH₂CPO] with transition metal ions Fe and Co, using a pH metric titration technique in 70% Dioxane-water mixture at three different temperatures (25 °C, 28 °C, and 30 °C) and at an ionic strength of 0.1M KNO₃. The method of Calvin and Bjerrum as adopted by Irving and Rossotti has been employed to determine metal-ligand stability constant logK values. It is observed that transition metal ion forms 1:1 and 1:2 complexes. The thermodynamic parameters such as, Gibb's free energy change (ΔG), entropy change (ΔS) and enthalpy change (ΔH) associated with the complexation reactions were calculated.

Keywords: Stability Constant, Transition metal, Hydroxy Substituted Chalcone, pH meter, Thermodynamic Parameters.

I. INTRODUCTION

The chemistry of chalcones has generated intensive scientific interest due to their biological and industrial application. Chalcones are natural biocides and are well known intermediates in the synthesis of heterocyclic compounds exhibiting various biological activities. Chalcones and their derivatives possess some interesting biological properties such as antibacterial, antifungal, insecticidal, anesthetic, anti-inflammatory, analgesic etc.

Stability of chalcone with metal complexes in biological system greatly responsible for the activity of chalcones against pathogenic bacteria and viruses. A stability constant (formation constant, binding constant) is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex, compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host-guest complexes and complexes of anions. The stability constant(s) provide the information required to calculate the concentration(s) of the complexes in solution. This study has many areas of application in chemistry, biology and medicine.

Temperature plays an important role in complex formation reaction. It affects on proton-ligand constant (pK) and metal-ligand stability constant (Log K). The stability constant of metal ion with number of ligand such as carboxylic acid, aldehyde, phenol, sulphonic acids, etc. are investigated by many workers¹

Thermodynamics of metal ion complex formation provides much significant information. In particular it is useful in distinguishing between enthalpy and entropic effect. Enthalpy effect depends on bond strengths and entropic effects have to do with changes in the order / disorder of the solution as a whole. The chelate effects are best explained in terms of thermodynamics. Mahajan. et al² have investigated the free energy change, entropy change and enthalpy change in formation of complex between Cu, Cd, Co, Ni, Pb and Zn metal ion and benzaldehyde thiosemicarbazone, pyridine 2-cabaldehyde in 50% dioxane-water mixture at 0.1 M ionic strength. Thakur et al.³ have studied the stability constant of Metformin Hydrochloride drug with rare earth metal ions La(III), Ce(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) using pH metric technique in 20% ethanol-water mixture at a three different

temperature. The stability constants of rhenium (V) metal complexes with selected medicinal drugs Adenosine (ADE), Isoniazid (ISO) and metformin hydrochloride (MET) in aqueous hydrochloric acid media and 0.2 M ionic strength at different temperature (293,303, 313 and 323 K) have been studied pH metrically by Gouda⁴. Rawate⁵ have studied stability constant and thermodynamic properties of complexation of Ibuprofen with Co(II) and Zn(II) pH metrically. Mishra⁶ have investigated the stability constant and thermodynamic parameters of trisubstituted pyrazolines with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) pH metrically.

METHOD & MATERIAL

Experimental Section:

An attempt has been made to study Co(II) and Fe(III) with BH₂CPO (L₄) ligand containing –OH group at a different temperature 25°C, 28°C and 30°C pH metrically. The data of stability constant (LogK) are used to evaluate the thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS).

pH-Metric Titration:

Calvin-Bjerrum pH-metric titration technique is used to carry out pH-metric titration at various temperatures 25°C, 28°C and 30°C.

- 1) Free acid HNO₃ (0.01M)
- 2) Free acid HNO₃ (0.01M) and ligand (20 x 10⁻⁴M)
- 3) Free acid HNO₃ (0.01M), ligand (20 x 10⁻⁴M) and metal ion (4 x 10⁻⁴M)

Against standard 0.1N NaOH solution.

The ionic strength of all the solutions 0.1M was maintained constant by adding appropriate amount of 1M KNO₃ solution. All the titrations were carried out in 70% Dioxane-water mixture and the reading were recorded for each 0.2 ml addition.

The titration are carried out by using pH-meter model EQ-614A maintained at constant temperature 25°C (298K), 28°C (301K) and 30°C (303K).

Thermodynamic Parameters:

The value of change in free energy ΔG, enthalpy ΔH and entropy ΔS for complex formation can be calculated using the temperature coefficient method and Gibbs Helmholtz's equation. The ΔG, ΔH and ΔS were determined for each chelate depending on their stability constant⁷. The free energy of complex formation (ΔG) of a complex is related to its stability constant by the relation.

$$\Delta G = -RT \ln K \quad \text{Or}$$

$$\Delta G = -2.303RT \log_{10}K \quad (1)$$

By rearrangement, we get,

$$\log_{10}K = -\Delta H / (2.303RT) + \Delta S / (2.303RT) \quad (2)$$

Where R- universal gas constant, T-absolute temperature and log₁₀K-stability constant of the complex. Enthalpy of complex formation (ΔH) and entropy of complex (ΔS) were calculated by plotting log₁₀K verses 1/T

We can specify the quantitative dependence of the stability constant on temperature from the relation⁸. An entropy change also plays an important role in complex stability.

Equation (2) is linear equation of the form y = mx + c,

Where y = log₁₀K, m = Slope = - ΔH/ (2.303RT), x = 1/T, C = intercept = ΔS/ (2.303RT).

After knowing the value of ΔG, ΔH we can easily calculate the entropy of reaction using Gibbs Helmholtz's equation.

$$\Delta G = \Delta H - T\Delta S \quad \text{or}$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (3)$$

II. RESULT & DISCUSSION

When the temperature increase, the value of proton-ligand stability constant (pK) decreases for all system. As temperature increases, the dissociation of ligand increases as result it gives more number of H⁺ ions and the dissociation constant increases, hence pK value decreases (pK = -logK).

The metal-ligand stability constant also decreases with increases in temperature, means when temperature increases, its stability decreases. It suggests that the complex formation is exothermic and favorable at lower temperature⁹. The negative values of ΔG indicate that the formation of complex is a spontaneous and thermodynamically stable process¹⁰. The more negative value of ΔG for metal complex indicates that non-electrostatic forces are stronger than electrostatic forces.

The negative value of ΔH indicates a decrease of enthalpy, due to the release of high energy water out of the drug cavity. The more negative value of ΔH becomes more stable in system. ΔH is known to be a measure of bond formed and bond broken in solutions. The negative values of ΔH indicate the complex formations are exothermic and more favorable at lower temperature. The ΔH values are negative and high, indicate that a very large change in total internal energy during complex formation towards stability.

The negative values of ΔS indicate the entropy is responsible for the association process¹¹. The decrease of entropy values during the formation of hydroxyls are attributed to an increase in the aggregation of molecules in these complexes.

Tables:

Table: 1- pK values of BH2CPO (L₄) at various temperatures

Temp	pK (Half Integral Method)	pK (Pointwise Method)
25° C	10.9982	8.5813
28° C	10.8152	8.5775
30° C	6.5995	6.1032

Table: 2- Determination of metal-ligand stability constant (LogK) of Co(II) and Fe(III) with BH2CPO (L₄) at 0.1M ionic strength at different temperatures

Ligand	Temp	Metal	LogK ₁	LogK ₂	LogK ₁ / LogK ₂	LogK ₁ .LogK ₂
L ₄	25° C	Co(II)	5.5394	2.2612	2.4497	3.2782
	25° C	Fe(III)	5.6133	1.9306	2.9075	3.6827
L ₄	28° C	Co(II)	5.1909	0.9075	5.7200	4.2834
	28° C	Fe(III)	5.5240	0.8250	6.6715	4.6790
L ₄	30° C	Co(II)	3.7271	0.0509	73.2239	3.6762
	30° C	Fe(III)	3.5127	0.4251	8.2632	3.0876

Table: 3- Comparative LogK₁ and LogK₂ at different temperature.

System		Temp=25° C		Temp=28° C		Temp=30° C	
Ligand	Metal Ion	LogK ₁	LogK ₂	LogK ₁	LogK ₂	LogK ₁	LogK ₂
L ₄	Co(II)	5.5394	2.2612	5.1909	0.9075	3.7271	0.0509
	Fe(III)	5.6133	1.9306	5.5240	0.8250	3.5127	0.4251

Table: 4- Thermodynamic Parameter Of The Complexes At 25°C, 28°C and 30°C Temperature

System		ΔG (KJ/deg)	ΔH (KJ/deg)	ΔS (KJ/deg)
Ligand	Metal Ion			
L ₄	Co(II)	-31607	-595954.8	-1890.01
	Fe(III)	-32028.6	-670590.4	-2136.82

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