



pH-Metric Study On Metal-Ligand Stability Constants Of Cu(II) And Ni(II) Complexes With Hydroxy Substituted Chalcone.

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Abstract : Stability constant is one of the very important concepts in coordination chemistry. Various Methods use to determine stability constant. In this present investigation is attempt to make the explain Proton-ligand stability constants and metal-ligand stability constants of reported ligand 1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2,4-dien -1- One (L₃) studied with transition metal ions like Cu(II) and Ni(II) were determine by pH-metric study at 0.1 M ionic strength. (30±1⁰C) in 70% Dioxane- water mixture by Bjerrum method as adopted by Calvin Wilson. 1:1 and 1:2 complexes were formed in between 1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2, 4-dien -1- One (L₃) and Cu(II) and Ni(II). Values of pK and log k were evaluated and compared from resultant data.

Keywords: Substituted chalcone, Dioxane – water mixture, stability constant

I.Introduction

Stability constants forehead plays a critical role in the identification and increase in efficiency of ligand design for selective complexation of metal ions in solution. Thus, it is important to assess the potential of metal-binding ligand organic in the complex formation process. During the complex formation in aqueous medium, two types of stabilities are considered, one is the thermodynamics stability, and the other is kinetic stability. This stability may be affected by various factors like nature of central metal ion and ligands, chelating effect, etc are useful for the determination of stability constants. Various modern techniques are used to determine the stability constant of simple as well as mixed ligand compound.

In the field of stability constants of organic ligands and their metal complexes the good contribution were given by Bjerrum¹ and Calvin². The measurement of stability constant of Ni (II) with substituted pyrazole carboxylic acid derivatives at temperature 298K is done in 70% DMF-Water mixture.³ M.W.Shaikh et al.⁴ studied Proton-ligand stability constants and metal-ligand stability constants of 1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one studied with inner transition metal ions like La(III), Sm(III) and Nd(III) were determine by pH-metric study at 0.1 M ionic strength.

The interaction of Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and Lu(III) metal ions with 2-hydroxy-(3,4-dioxymethylene)-5-methyl chalcone and 2-hydroxy-5-methyl-4-methoxy chalcone have been investigated by pH-metric technique at 0.1 M ionic strength at 27 ± 0.1 °C in 70 % dioxane-water mixture⁵. R.B. Dhake⁶ investigated the metal-ligand and proton–ligand stability constant of Ce(III) with Clobetasol propionate was determined at various ionic strength by pH metric titration . R.P Giram et al.⁷ have studied the stability constants and thermodynamic parameters of transition metal complexes of substituted aminothiazole Schiff bases. Thorat et al.⁸ have been studied The complex formation between Pr (III) & Sm (III) metal ions and 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(3-nitrophenyl) isoxazoline, 3-(2-hydroxy-3-nitro-5-methylphenyl)-5-(4-chlorophenyl) isoxazoline, 3-(2-hydroxy-3-nitro- 5-methylphenyl)-5-(2-furyl)isoxazoline. Thakur et al.⁹ studied the complex formation between Cu(II), Ni(II) & Co(II) metal ions with 1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one and 1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one chalcones at 0.1M ionic strength (26±1⁰C) in 70% Dioxane-water mixture by Bjerrum method as adopted by Calvin Wilson. Recently measured stability constant of inner transition metal ions with 1-(5-bromo-2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one at 0.1 M ionic strength by pH metrically¹⁰.

II. Experimental methodology

1.1 Material and Methods

All chemicals used are of AR grade. The ligand (L₃) was synthesized in the laboratory by reported protocol¹¹. The stock solution of the ligand was prepared by dissolving required amount of ligand in a 70% (Dioxane + water) mixture.

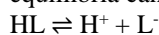
1.2 General procedure

Types of Titrations

i) Free acid HNO₃ (0.01 M)

ii) Free acid HNO₃ (0.01 M) and ligand (20 x 10⁻⁴M)

iii) Free acid HNO₃ (0.01 M) and ligand (20 x 10⁻⁴) and metal ion (4 x 10⁻⁴M) against standard 0.1N NaOH solution. The ionic strength of all the solutions was maintained constant 1M by adding appropriate amount of KNO₃ solution. All the titrations were carried out in 70% (Dioxane+water) mixture and the reading were recorded for each 0.1 ml addition. The graph of volume of alkali added (NaOH) against pH were plotted. The ligand involved in the present work may be considered as a monobasic acid having only one dissociable H⁺ ion from phenolic -OH group and it can therefore, be represented as HL. The dissociating equilibria can be shown as.



By the law of mass action, we have,

$$K = [HL] / ([H^+] [L^-]) \quad (1)$$

Where, the quantities in bracket denote the activities of the Species at equilibrium.

III. Result and Discussion

2.1 Calculation of Proton-Ligand Stability Constant (n_A)

The plots between volume of NaOH and pH of the solution were used to determine the proton ligand stability constant (representing the replacement of H⁺ ions from functional group of ligand with respect to pH value). The horizontal difference (V₂-V₁) was measured accurately between the titration curves of free acid and acid + ligand. It was used to calculate the formation number n at various pH values and fixed ionic strength μ = 0.1 M using Irving and Rossotti's equation [1, 2].

$$n_A = \gamma \frac{(E_0 + N) (V_2 - V_1)}{(V_0 + V_1) T_L^0} \quad (2)$$

Where, V⁰ is the initial volume of the solution. E⁰ and T_L⁰ are initial concentrations of the mineral acid and ligand respectively. V₁ and V₂ are the volumes of alkali of normality N during the acid and ligand titration at given pH. γ is the replaceable proton from the ligand. The data of n_A obtained at various pH along with the horizontal difference for some representative systems are represented in Table 1. The metal ligand Ligand formation number (n) is estimated by Irving-Rossotti's equation.

$$n = \frac{(E_0 + N) (V_3 - V_2)}{(V_0 + V_2) T_m^0} \quad (3)$$

Where, the notations have the same meaning as given in earlier equation. The horizontal difference (V₃-V₂) between the metal complex (A+M+L) and reagent (A+L) curve is used to evaluate the value of n using Irving Rossotti's equation.

Table 1 Proton ligand stability constant (pK)

Ligand	System	pK	
		Half integral method	Point wise method
L3	1-(5-bromo-2-hydroxyphenyl)-5-phenylpenta-2,4-dien -1- One	7.7871	6.4506

Table 2: Metal-ligand stability constant (log K)

System	LogK ₁	LogK ₂	Δ LogK
Cu(II)+L ₃	5.5300	3.0986	2.4314
Ni(II)+L ₃	5.0963	2.6668	2.4295

Conclusion

From the titration curves, it is observed that the departure between acid + ligand (A+L) curve and acid + ligand + metal (A+L+M) curve for all systems started from pH 3.6 this indicated the commencement of complex formation. Also change in colour from yellow to orange in the pH range from 3.9 to 8.6 during titration showed the complex formation between metal and ligand.

The difference between $\text{Log}K_1$ and $\text{Log}K_2$ is less than 2.5, indicating the simultaneous formation of 1:1 and 1:2 complexes when the difference is more than 2.5, then in such a case a stepwise complex formation takes place¹². From the table 2, it is observed that the difference between $\text{log} K_1$ and $\text{log} K_2$ values are not sufficiently large that indicates the simultaneous formation of complex between metal ions and ligand. Cu (II) - L3 and Ni (II)-L3 forms simultaneous formation of 1:1 and 1:2 complexes.

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REFERENCES

- [1] Bejerrum J.1941. Metal Ammine formation in aqueous solution, Copenhagen, Denmark: P. haase and son, 296.
- [2] Calvin M, Wilson KW. 2003. Stability of chelate compounds, J Am. Chem. Soc, 1945, 67.
- [3] Jagtap V. S. 2019. Determination of Stability Constant of Some Coordination Compound By pH Metric Technique. Pramana Research Journal, 9 (8): 22-29.
- [4] Shaikh, M.W, Thakur, S.D, Bansod, S.B, Kakade K.P, Pimple, S.G. 2020. pH-Metric Measurements of Hydroxy Substituted Chalcone with Some Inner Transition Metal Ions At 0.1M Ionic Strength. UPA National Peer-Reviewed e-journal, 3: 346-351.
- [5] Tambatkar, G.D, Meshram, Y.K, Gadpayale, M.R. 2008. Stability Constants of Lanthanides (III) Chelates with Substituted Chalcones. Asian Journal of Chemistry, 20(7): 5414-5418.
- [6] Dhake, R.B. 2018. Studies on Thermodynamic Stability of Constant of Clobetasol Propionate with Ce(III) Complex. Journal of Applicable Chemistry, 7(5): 1461-1465.
- [7] Giram, R.P, Muthal, B.N, More, P.G. 2019. The study of stability constants and Thermodynamic parameters of transition metal complexes of substituted aminothiazole Schiff Bases. The Pharma Innovation Journal, 8(1): 249-252.
- [8] Thorat, S.A, Thakur. S.D. 2015. Metal ligand stability constant of substituted 3, 5-Diaryl isoxazolines complexes in 70% dioxane solvent media. J. Curr. Chem. Pharm. Science, 5(2): 67-74.
- [9] Thakur, S.D, Shaikh, M.W. 2019. Studies of metal ligand stability constant of hydroxy Substituted chalcone complex in 70% dioxane solvent media pH metrically. Technical Research organisation india, 6(1): 356-359.
- [10] Thakur, S.D, Shaikh, M.W, Puri, K. N. 2021. Studies of some inner transition metal ions Complexes with hydroxyl Substituted chalcone complex at 0.1 M Ionic strength. Vidyabharati International Interdisciplinary research journal, 8: 22-24.
- [11] Swapnil, K.W, Kakade, K.P. 2013. Synthesis and characterization of substituted 5-bromo- 2-benzylidene-1-benzofuran-3-one and its structural determination. International Journal of chemical and pharmaceutical science, 4(3): 119-122.
- [12] Deolankar, D. S, Deshpande, Y.H. 1987. La(III), Pr(III), Gd(III), Tm(III) and Dy(III) Complexes of aryl furyl and aryl thienyl β -diketones. Indian Journal of Chemistry, 26(A): 68-69.