



Metal-Ligand Stability Constants of Co(II), Ni(II), Cu(II) Metal ion Complexes with Substituted Ketones & Simple Ketones at 0.1M Ionic Strength pH Metrically

KEYWORDS

2-Hydroxy-4-Methyl-5-Chloro Acetophenone, Benzophenone, DMF water mixture, Stability constant.

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ABSTRACT *The interaction between Co(II), Ni(II) and Cu(II) Metal Ions and 2-Hydroxy-4-Methyl-5-Chloro Acetophenone (L1) and Benzophenone have been studied at 0.1M Ionic Strength in 70% DMF water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Co(II), Ni(II) and Cu(II) Metal ions form 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants ($\log k$). From estimated data (pK and $\log k$), the effects of substituents were studied.*

INTRODUCTION

Considerable research work has been done on the study of complexes in solution in last five decades. The development in the field was initiated by Jannik, Bjerrum project¹ published in 1941, Calvin, Bjerrum, Irving, Rossotti, Martell and Schwarzenbach have made important contributions to the rapid progress in our understanding of metal complex in aqueous as well as in mixed solvent.

Rossotti and Rossotti¹ have define a complex as a species formed by the association of two more simple species each capable of independent existence, when one of the simple species is a metal ion the resulting entity is known as metal complex.

The term ligand some time applied to the particular atom in the molecules by means of which the molecules is attached to the central metal atom or it may be applied to the molecules as whole some ligand are attached to the metal atom more than one doner atom in such a manner as to formed heterocyclic ring. This is known as chelation. The chelates have been extensively studied in solution as well as in solid state by many workers, because of their remarkable properties and high stability. The extensive work in co-ordination complexes have been made possible with the help of various experimental techniques and has led in number of empirical conclusions which have been detailed by Martell². The stability of complex in a solution is governed by the nature of central atom and the ligands. The most important characteristics of the central atom which influence the stability of complex compound are the degree of oxidation (charge on the central atom in case of ionic complexes) the radius and electronic structure in the case of complexes with monoatomic ligand, stability is dependent on the same characteristic in the ligand as considered for the cation. The strength of bonding for ligand molecules and poly atomic ions depends in addition on the nature of atom directly link to the particular features of the structure of ligand molecules or ions.

The complex formation is favored by negative enthalpy and positive entropy change it is very difficult to predict the contribution on these terms because of solution of the constituents of complex also must be taken into consideration. According to Williams¹ entropy term usually favorable when ligand is anionic and is generally unfavorable in case of neutral ligands. Enthalpy change in complex formation is generally determined by

- Temperature coefficient method.
- Microcolorimetry.

The second method is more sensitive and gives more accurate results have been used by a hundred of workers to determine H of various complexes transition metal ion and lanthanides.

The stability of complex also depends upon the size and number of chelating ring. The size of chelating ring and number of the rings formed on chelation are determine by the structure of chelating agent. Hence the stability of the chelate depends on both the factors.

Ley³ has concluded from his work on amino acid chelates that five and six membered rings are most stable. Since then much evidence has accumulated to prove that all chelates have either five or six membered rings.

Chelation as well as stability is governed by nature of metal. Nature of metal ion also plays an important role in chelation and stability of complexes.

Stability order of metal ions transition metal ions is found by Irving and Williams⁴ by comparing the ionic radius and second ionization potential of the metal ions because it is valid for most nitrogen and oxygen doner ligands.

This order was rationalized as $Co^{2+} < Ni^{2+} < Cu^{2+}$ In the present work especially effects of trivalent metal ion such as Ce(III), Pr(III), Tb(III) on the properties of complexes is studied.

Metal, ligand stability constant of complexes of transition metal ions, lanthanides and unclear metal ions with dihydroxy compounds, amino hydroxyl phenols, naphthols, triazines an peptiedes have been reported by number of workers⁵.

Effect of ligand on stability of some diketones is studied by Bhargava et al⁶. Stability and distribution constant for Pr(III) acetylaceton complexes are studied by Lundvist and Robert⁷.

However the detailed study of complexes with some substituted ketone and simple ketone under the identical set of complexation is still lacking.

[Considerable research work has been done in the past, on the study of complexes². Irving and Williams⁴ had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionization potential of metal ions, as it is valid for most nitrogen and oxygen donor ligand. Narwade et al³¹ have investigated metal-li-

gand stability constant of some lanthanides with some substituted sulphonic acids. Bodkhe et al²⁴ have reported the metal-ligand stability constants of some diketones. Tekade et al²⁵ investigated stability constant of some substituted pyrazolines, isoxalline and diketone. Shekhon⁷ potentiometrically determined proton-ligand stability constants in various aqueous organic mixtures. Prasad²⁶ studied the stability of same metal complexes of β -diketones. Deosarkar²⁷ have studied stability constants of Al(III), Cr(III) and Fe(III) metal ion complexes with substituted sulphonic acid. Pund²⁸ have investigated interaction between La(III) and Nd(III) metal ions and 1-(4-hydroxy-6-methylpyrimidine)-3-substituted thiocarbamide of 0.1M ionic strength pH metrically. Recently speciation of binary complexes of Ca(II), Mg(II) and Zn(II) with L-glutamic acid in DMSO-water mixtures has been studied³⁰.]

The present paper describe the interactions between Co(II), Ni(II) and Cu(II) Metal ions and 2-Hydroxy-4-Methyl-5-Chloro Acetophenone [C₉H₇O₂Cl] (L₁) and Benzophenone [C₁₃H₁₀O] (L₂) have been studied at 0.1 M Ionic strength in 70%DMF-water mixture at (30 ± 0.1) by Bejerrum pH metric method as adopted by Calvin and Willson.

MATERIALS AND METHODS

The ligand 2-Hydroxy-4-Methyl-5-Chloro Acetophenone [C₉H₇O₂Cl] (L₁) and Benzophenone [C₁₃H₁₀O] (L₂) were synthesized in the laboratory by known literature method. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points. The stock solution of the ligand was prepared by dissolving required amount of ligand in a minimum of volume of DMF(Di methyl formamide) subsequently diluted to final volume.

The solution of sodium hydroxide (E.Merck) was prepared free from carbonate by allowing the solution to stand for a long time till any carbonate, if present, precipitated. The solution was filtered through a sintered glass crucible and kept in a pyrex vessel free from carbon dioxide and was used as the titrant for the pH-metric titrations. The solution of sodium hydroxide was standardized by titrat in against standard oxalic acid solution before starting an experiment.

Nitric acid of Ridel (Germany Quligen) was used for preparation of stock solution its exact normality was calculated by titrating against standard sodium hydroxide.

Potassium nitrate (E Merck) was dissolved in carbon dioxide free distilled water 1 M potassium nitrated solution was used in the present investigation.

Metal Nitrates :- Rafe earth nitrates (Anala-R quality) 1) Cobalt nitrates 2) Nickel nitrate 3) Copper nitrate were used. The metal content in the solution was estimated gravimetrically all metal ions.

The substituted Ketones and simple Ketones :-

- 1) 2-Hydroxy-4-Methyl-5-Chloro Acetophenone
- 2) Benzophenone.

pH-meter and Measurements :-

All the pH-measurement and titration are carried out with pH-meter L1-L10T (Elicomake) accuracy 0.01 with a glass and calomel electrode assembly.

The instrument could read pH in the range 0.0 to 14.00 in step of 0.005 this pH-meter has a built in internal electronic voltage stabilizer for -10% fluctuations in voltage supply with temperature compensator converting the range 0.00 to 100.00°C. The pH meter was switched on half an hour before starting the titration for the initial warm up of the instrument.

Before making any measurement with the meter the electrodes were washed with distilled water and dried with filter paper. The reading were record only when the instrument registered a steady value for at least one minute. The pH-

meter was standardized before each titration with a buffer solution of pH 4.01, 7.00 and 9.15.

All the glass used in these experiments were of pyrex quality. The consumption of alkali during the titration was from a microburette giving an accuracy of 0.014 ml. the microburette which was graduated to 0.01 ml. was calibrated by method described by vogel¹⁴.

Procedure

The experimental procedure involved the titration of

- 1) Free acid HNO₃ (1x 10⁻²m)
- 2) Free acid HNO₃ (1x10⁻²m) & ligand (20 x 10⁻⁴m)
- 3) Free acid HNO₃ (1x 10⁻²m) & ligand (20x10⁻⁴) & metal salt (4x10⁻⁴m) against standard carbonate free sodium hydroxide (NaOH) 0.1 N were carried out in 70% DMF +water.

Titration were carried out by adding an appropriate of (0.1 M HNO₃) solution ionic strength of the solution was maintain determined in the present investigation.

- 1) pK value of substituted ketone and simple ketone in 70%DMF water medium.
- 2) Log K value of metal ion Cu(II),Ni(II), Co(II) chelates with substituted ketone and simple ketone .

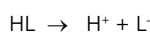
The graph are plotted between pH of the solution and ml of the alkli (NaOH) added for the system.

There curve is designated as.

- 1) Acid titration curve (A).
- 2) Acid +Ligand it curve (A+L)
- 3) Acid +Ligand + metal curve (A+L+M).

RESULTS AND DISCUSSION

Substituted ketone and simple ketones may be considered as monobasic acid having only one replaceable H⁺ ion from -OH group that -OH generally dissociates completely above pH 9.00 and can therefore be represented as.



The titration data were used construct the curves between volume of NaOH Vs pH . they are called acid - ligand and metal titration curves.

It is observed from titration curves for all the systems that ligand curves start deviating from the free acid (HNO₃) curves at about pH 5.5 and deviated continuously up to pH 11 the deviation shows that dissociation of -OH group in substituted ketone and simple ketones.

The average number of proton associated with the ligand (\bar{n}_A) was determined from acid and ligand titration curves employing the equation of Irving and Rossotti⁷. The proton ligand formation number n_A were calculated by Irving and Rossotti expression (table 2)

$$\bar{n}_A = \frac{(E_0 + N)(V_2 - V_1)}{(V_0 + V_1) T_L^0} \quad \text{-----(1)}$$

Where ; N is the concentration of sodium hydroxide (0.133 mol dm⁻³), (V₂ - V₁) is the measure of displacement of the ligand curve relative to acid curve, where V₂ and V₁ are the volume of alkali added to reach the same pH reading to get accurate values of (V₂ - V₁); the titration curves were drawn on an enlarged scale; E⁰ and T_L⁰ are the resultant concentration of nitric acid and concentration of ligand, respectively. V₀ is the initial volume of reaction mixture (50 cm³). Proton-ligand stability constant pK values of ligand were calculated by algebraic method point wise calculation and also, estimated

from formation of curves (fig 3 , 4) \bar{n}_A Vs pH (Half integral method) by noting pH at which $n_A = 0.5$ [Bjerrum 1957] (table 1).

Metal-ligand stability constant (log k) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

$$n = \frac{(E_0 + N)(V_3 - V_2)}{(V_0 + V_2) T_m^0} \quad \text{-----(2)}$$

Where N , E_0 , V_0 and V_2 have same significance as in equation (2), V_3 is the volume of NaOH added in the metal ion titration to attain the given pH and T_m^0 (4×10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture. The stability constants for various binary complexes have been calculated (Table 3).

CONCLUSION

From the titration curves, it is observed that the deviation between (Acid +Ligand) curve & (Acid + Ligand + Metal) curve for all system of ligand-1 started from pH 2.6 to 3.7 and of ligand-2 started from pH 2.5 to 2.9 , this indicate the commencement of complex formation. It could be seen from table (3) the logk values of ligand-1 is greater than logk values of ligand-2. This is due to effect of electron releasing group $-CH_3$ and electron withdrawing group $-COCH_3$, $-NO_2$ etc. Also change in color from yellow to brown in pH range from 3.0 to 9.0 during the titration showed the complex formation between Metal & Ligand.

Proton ligand stability constant (pk):-

It is observed from titration curve in (fig 1,2) that ligand curves starts deviating from the free acid (HNO_3) curves at about pH > 2.5. and deviated continuously up to pH 11 the deviation shows that dissociation of $-OH$ group in substituted ketone and simple ketones. pk values of ligand no.1 is greater than ligand no.2 this may be due to the effect of stronger electron withdrawing group $-COCH_3$ and Cl group that reduces the pk values but increase the dissociation.

In case of simple ketone and simple ketone pk values is lesser than substituted ketone this is due to the effect of $-CH_3$ electron releasing group that decreased the dissociation and increase the dissociation constant, pk values are found to increase in the following order of ligand

Ligand-1 > Ligand-2

Table no 1:- Proton – Ligand Stability constants (pK)

Sr. No	System	pK	
		Half Integral method	Pointwise calculation method
1)	2-Hydroxy-4-Methyl-5-Chloro Acetophenone	10.20	10.20
2)	Benzophenone	8.70	8.70

Table 2 :- Proton-Ligand formation number (\bar{n}_A) at 27°C and ionic strength $\mu = 0.1$ mol. dm^{-3} , Medium= 70%Solvent $T^0 = 20.00 \times 10^{-4}$, $T_m^0 = 4 \times 10^{-4}m$, $V_0 = 50$ ml, $N = 0.20$ N, $E^0 = 1.0 \times 10^{-2}$ ml.

pH	V_1	V_2	$V_2 - V_1$	\bar{n}_A
5.0	1.14	1.2	0.06	0.872
5.5	1.18	1.26	0.08	0.8279
6.0	1.24	1.32	0.08	0.8277
6.5	1.26	1.4	0.14	0.6984

[2- Hydroxy-4-Mythyl-5-Chloro Acetophenone] L1

7.0	1.36	1.48	0.12	0.7409
7.5	1.4	1.52	0.12	0.7407
8.0	1.46	1.62	0.16	0.6539
8.5	1.52	1.70	0.18	0.6102
9.0	1.58	1.78	0.20	0.5663
9.5	1.64	1.84	0.20	0.5658
10.0	1.72	1.94	0.22	0.5216
10.5	1.78	1.02	0.24	0.4774
11.0	1.84	2.1	0.26	0.4332

[Benzophenone] L2

pH	V_1	V_2	$V_1 - V_2$	\bar{n}_A
5.0	1.12	1.2	0.08	0.8282
5.5	1.18	1.26	0.08	0.828
6.0	1.22	1.32	0.1	0.7848
6.5	1.24	1.36	0.12	0.7416
7.0	1.26	1.42	0.16	0.6554
7.5	1.30	1.48	0.18	0.612
8.0	1.32	1.52	0.2	0.5687
8.5	1.34	1.56	0.22	0.5253
9.0	1.36	1.6	0.24	0.482
9.5	1.40	1.66	0.26	0.4383
10.0	1.48	1.76	0.28	0.3341
10.5	1.54	1.84	0.3	0.35
11.0	1.66	1.98	0.32	0.305

Metal-Ligand stability constant (Log K):-

It is observed that (table 3) sufficiently large difference between $\log K_1$ & K_2 Values indicates the stepwise formation of complex between metal ion and ligand except Co(II) and Cu(II) for ligand-1. It showed that less difference between $\log K_1$ & $\log K_2$ values indicates Co(II) – Ligand -1 & Cu (II) – Ligand -1 complexes are occurring simultaneously.

The values of $\log K_1$ & $\log K_2$ for Ni (II) – Ligand -1 & Ligand -2 complexes are higher than Co(II) & Cu(II) –Ligand -1 and Ligand -2 complexes, indicate that Ni (II) forms more stable complexes with ligand 1 and ligand 2 than Co(II) and Cu(II) metal ions.

The higher value of ratio ($\log K_1 / \log K_2$) for Ni(II) & Cu(II) – Ligand -2 complexes indicates the more stable stepwise complex formation as compare to Co(II) & Cu(II) – Ligand 2 complexes.

Table 3 : Metal – Ligand Stability constants (log K)

System	Log K_1	Log K_2	Log $k_1 - \log K_2$	Log $K_1 / \log K_2$
Co(II) L1	6.00	5.04	0.96	1.19
Ni(II) L1	6.20	4.6	1.6	1.34
Cu(II) L1	6.10	4.5	o.7	1.12
Co(II) L2	6.2	5.2	1.00	1.19
Ni(II) L2	6.40	4.8	1.6	1.33
Cu(II) L2	6.30	4.9	1.4	1.28

Fig 1 & 2: pH against volume of NaOH at $\mu=0.1M$ at $(30\pm 0.1)^\circ C$

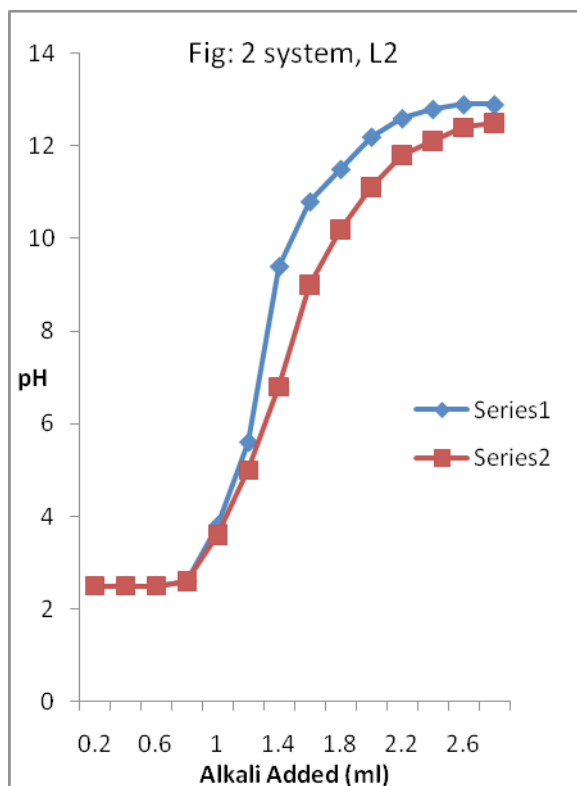
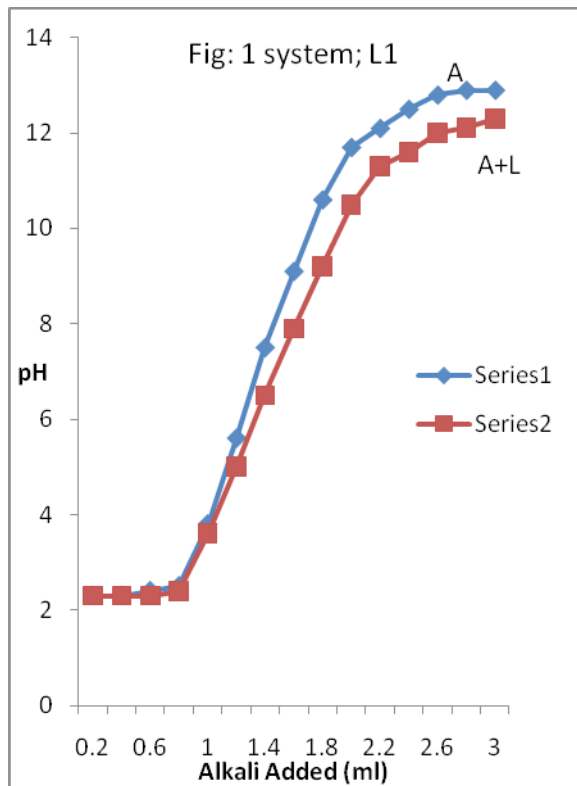
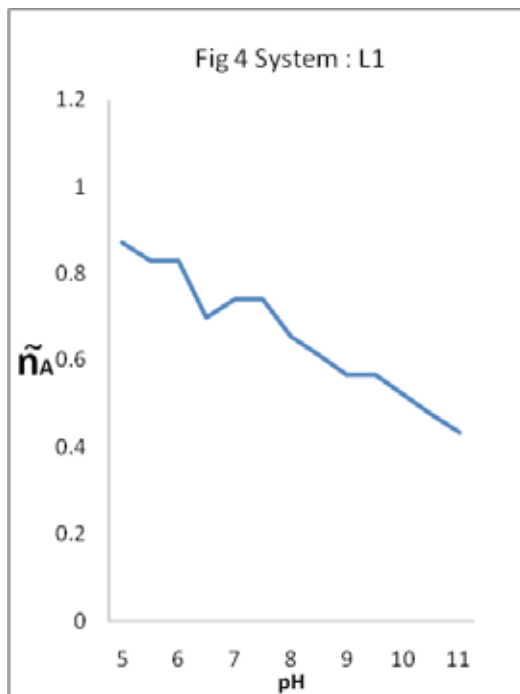
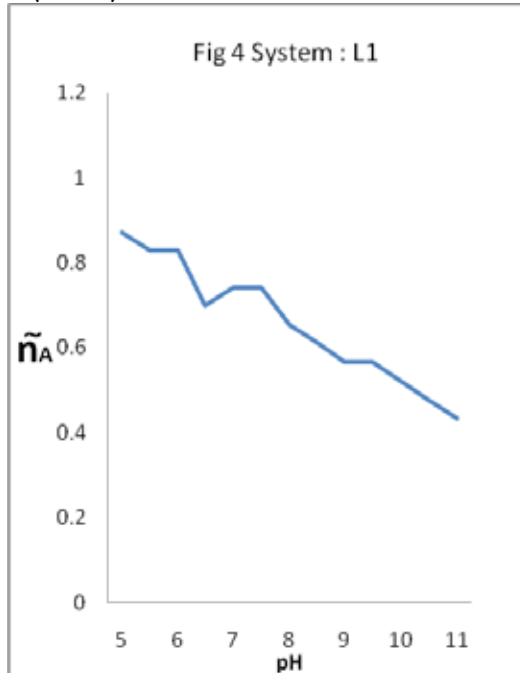


Fig 3 & 4 : Formation curves of \tilde{n}_A against pH at $\mu=0.1M$ at $(30\pm 0.1)^\circ C$



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