International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.11 pp 403-412, 2015

A Thermodynamic and comparative study of complex formation of N-Benzothiazol-2-yl-3,5-disubstituted pyrazolines with some transition metals by conductometry and pH-metry

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Abstract: The complexometric reaction between Co(II), Ni(II), Cu(II) with 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-methoxy phenyl) pyrazoline(L^1), 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-phenyl pyrazoline(L^2), 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-chloro phenyl) pyrazoline(L^3), 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-(4-methoxy phenyl) pyrazoline(L^4), 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-(4-chloro phenyl) pyrazoline(L^5) and 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-phenyl pyrazoline(L^6) have been studied by Conductometric method. N-Benzothiazol-2-yl-3,5-disubstituted pyrazolines forms 1:1 complexes with Co^{2+}, Ni^{2+}, Cu^{2+} cations in solutions. The stability of these complexes was calculated by conductance measurement by using Modified Job's Method. The analysis has been carried out by using Conductometry and pH-metry. On the basis of Modified Job's Method, thermodynamic parameter Gibbs free energy also obtained for above complexes.
Key Words: Stability constants, N-Benzothiazol-2-yl-3,5-disubstituted pyrazoline, Co(II), Ni(II), Cu(II) , Thermodynamic parameter, Conductometry.

1.Introduction :

The presence of another group or atoms like O,N,S created a heterocyclic compound, having wide applications in pharmaceutical chemistry[1-2]. Pyrazolines are derived from pyrazoles but being an heterocyclic compound, pyrazoline have an tremendous applicability. As known that compounds made by heterocyclic atoms are generally acts like a drugs having various types of activities. Hence pyrazoline considered as therapeutic agent[3]. Like that substituted pyrazolines also shows biological activities like antimicrobial[4-6], antiinflammatory[7-8], anticancer[9], antitumor[10], antidiabetic[11], anti-HIV[12] etc. It also has special importance in biochemical systems.

Some pyrazoline derivatives shows bacterial[13] and fungicidal[14] activity.

The various types of physical-chemical techniques are used for the complexometric study like pH-metry[15], potentiometry[16], conductometry[17], polorography[18], spectrophotometry[19], ion exchange[20] etc.

Out various techniques, conductometry technique is considered as a more accurate because it shows high precious at extremely low solution concentrations where the interactions between cation and anion are known to be very small. In addition, conductometry is a highly sensitive and inexpensive technique with a simple experimental arrangements.

Many metal-containing compounds, especially those of transition metals are coordination complexes. Coordination complexes are so pervasive that the structure and reactions are described in many ways.

The affinity of metal ions for ligands is described by stability constant and also referred as formation constant.

Formation constant vary widely, large values indicate that the metal has high affinity for the ligand, provided the system is at equilibrium. When complex ions forming in solutions they also play a key role in solubility of other compounds. When a complex ion is formed it can alter the concentrations of its components in the solution.

As a whole stability constant is a measure of the strength of the interaction between the reagents that come together to form the complex.

The thermodynamics of metal ion complex formation provides much significant information. In particular it is useful in distinguishing between enthalpic and entropic effects. Enthalpic effects depend on bond strengths and entropic effects have to do with changes in the order/disorder of the solution as a whole.

Literature survey reveals that the conductometry and thermodynamic study of complex formation is also studied by various reserchers[21-27].

While comparative study of determination of formation constants with potentiometry and pH-metry was carried out by using traditional methods[28-30].

In the present investigation, formation constants of transition metal ions Co(II), Ni(II), Cu(II) with 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-methoxy phenyl) pyrazoline(L^1), 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-phenyl pyrazoline(L^2), 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-chloro phenyl) pyrazoline(L^3), 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-(4-methoxy phenyl) pyrazoline(L^4), 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-(4-chloro phenyl)pyrazoline(L^5) and 1-Benzothiazol-2-yl-3-(2-hydroxy-5-methyl phenyl)-5-phenyl pyrazoline(L^6) in 1:1 ratio at 28 ± 0.1^0C. For this study, Modified Job's Method was used. The ionic strength was maintained constant at 0.1M.

The Modified Job's Method generally used for the synthesis and characterization of some transition metal complexes[31-33].

The comparative study of formation constants of complexes has been done by two analytical techniques as conductometry and pH-metry further both the techniques were implemented for thermodynamic parameter determination.

2.Experimental :

2.1 Reagents And Solvents :

The ligands were synthesized by the microwave assisted method. The purity of the compounds are checked by analytical and spectral analysis i.e. melting point determination, IR, and NMR spectra. All chemicals were used of AR grade i.e. metal nitrates.AR grade acetone was used as a solvent. The stock solution of the metal nitrates and ligands in acetone were prepared by the water and solvent in a minimum volume of mixture.

0.02M, 0.005M, 0.0025M of metal solution were prepared by dissolving the requisite quantities in conductivity water.

Similarly, ligand solution of 0.01M, 0.005M and 0.0025M concentration were also prepared in acetone.

2.2 Apparatus :

The conductance measurement were performed by using conductometric instrument EQUIP-TRONICS conductivity meter model no. EQ.665 equipped with a combined conductivity cell. The instrument is calibrated by adjusting 1.00mƱ on conductometer before each titration. The model EQ-621). All the weighing were done on electronic balance [Contech CB-series with accuracy ±0.001]. A conductometric cell with a cell constant of 1 was used throughout the study.

2.3 Methods :

For the conductometric titrations, two methods were used

2.3.1. Monovarient Method :

For the detection of Metal-Ligand ratio the monovarient method was used to determine the stoichiometry of the complex systems and firstly given by Nayar and Pande.

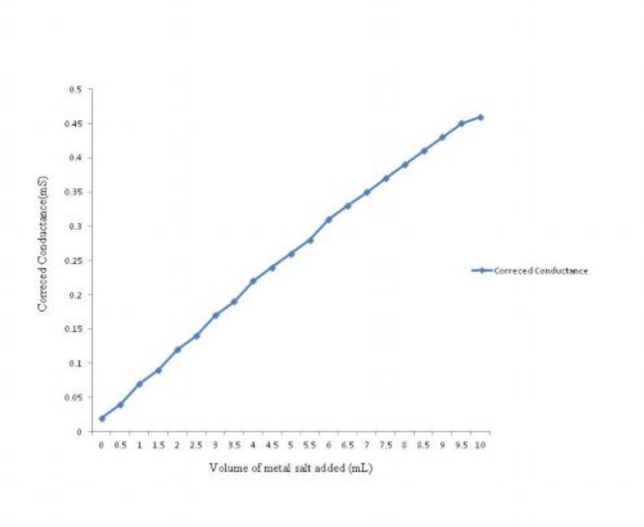
For this method the stock solution of ligand solution of 0.01M concentration in acetone-water mixture was prepared. Similarly, metal salt solution of 0.02M was prepared in conductivity water. These stock solutions were taken for the further dilution.

Out of total, 5ml of stock solution of ligand solution was diluted upto 50ml in a beaker and kept at thermostatic bath at 25^0C.This was titrated against 0.02M metal salt solution conductometrically. Conductance was recorded after every addition of 0.5 ml of metal salt solution with constant stirring at constant temperature. Conductance can be calculated as

Conductance = {(V+v)/V}*(Observed conductance) -------------------- (I)

Where, V= initial volume of ligand solution,

v = volume of metal solution added.



Graph I : Conductometric titration between 1-Benzothizol-2-yl-3-(2-hydroxy phenyl)-5-(4-chlorophenyl) pyrazoline (L^3) with $Co(NO_3)_2.6H_2O$

The reported conductometric data is presented in table (**Table I).**

Table I : Conductometric titration between 1-benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-chlorophenyl) pyrazoline (L^3) + $Co(NO_3)_2.6H_2O$

S.N.	Volume of metal salt added (ml)	Observed Conductance(mS)	Corrected Conductance(mS)
1	0	0.02	0.02
2	0.5	0.04	0.0404
3	1	0.07	0.0714
4	1.5	0.09	0.0927
5	2	0.12	0.1248
6	2.5	0.14	0.147
7	3	0.17	0.1802
8	3.5	0.19	0.2033
9	4	0.22	0.2376
10	4.5	0.24	0.2616
11	5	0.26	0.286
12	5.5	0.28	0.3108
13	6	0.31	0.3472
14	6.5	0.33	0.3729
15	7	0.35	0.399
16	7.5	0.37	0.4255
17	8	0.39	0.4524
18	8.5	0.41	0.4797
19	9	0.43	0.5074
20	9.5	0.45	0.5355
21	10	0.46	0.552

The equivalence point was determined from graph which reflects 1:1 composition of metal and ligand.

2.3.2. Continuous Variation Method :

For the determination of composition and stability constant of complexes Modified Job's Method was implemented. For this solution, both metal salt and ligand solution was taken in equal concentration. These solutions then separated in three series i.e. C1, C2 & C3 for the determination of conductance. In set C1 metal solution is added from 0.0ml to 10ml quantity so that total solution that made was of 10ml. Similarly C2 set was filled with ligand solution from 0.0ml to 10ml and C3 set was also having metal and ligand both the solutions to filled total 10ml quantity from 0.0ml to 10ml.

Conductance was recorded for each solution. Conductance was calculated as 'C1+C2-C3'[34]. Graphs were plotted between conductance and mole metal-ligand ratio. The same procedure was repeated for another concentration. The graph was plotted as conductance of both concentrations taken on one axis and mole ratio on another axis. On the basis of equivalence point, the composition and stability constants for the complexes were determined.

The results were presented in tables **Table II(i) & Table II(ii).**

Table II (i) : Conductance of 1-Benzothiazol-2-yl-3-(-2-hydroxy-5-methyl phenyl)-5-(4-chlorophenyl) pyrazoline (L^3) with $Co(NO_3)_2.6H_2O$.

Concentration of metal – 0.005M, Concentration of ligand – 0.005M

S.N.	Ratio	M:S (C1)	S:L (C2)	M:L (C3)	Conductance (C1+C2-C3)
1	0:10	0.00	0.029	0.00	0.029
2	1:9	0.05	0.028	0.04	0.038
3	2:8	0.10	0.031	0.07	0.061
4	3:7	0.16	0.031	0.11	0.081
5	4:6	0.20	0.031	0.14	0.091
6	5:5	0.26	0.032	0.18	0.113
7	6:4	0.33	0.034	0.26	0.102
8	7:3	0.42	0.034	0.36	0.094
9	8:2	0.51	0.034	0.47	0.074
10	9:1	0.60	0.033	0.56	0.073
11	10:0	0.67	0.035	0.65	0.055

Table II (ii) Concentration of metal – 0.0025M, Concentration of ligand – 0.0025M

S.N.	**Ratio**	**M:S (C1)**	**S:L (C2)**	**M:L (C3)**	**Conductance (C1+C2-C3)**
1	0:10	0.00	0.029	0.00	0.029
2	1:9	0.02	0.030	0.02	0.030
3	2:8	0.04	0.032	0.04	0.032
4	3:7	0.07	0.033	0.07	0.033
5	4:6	0.09	0.033	0.09	0.033
6	5:5	0.13	0.032	0.12	0.042
7	6:4	0.17	0.035	0.18	0.025
8	7:3	0.22	0.036	0.24	0.016
9	8:2	0.28	0.036	0.30	0.016
10	9:1	0.40	0.037	0.42	0.017
11	10:0	0.50	0.034	0.52	0.014

The graphs plotted from the results shows 1:1 ratio of metal- ligand.

2.4 Synthsis of N-Benzothiazol-2-Yl-3,5-Disubstituted Pyrazoline with Transition Metal :

For the synthesis of complex ligand 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-chlorophenyl) pyrazoline (L^3) is taken with Co(II) metal ion.

Equimolar solutions of metal and ligand were prepared and were mixed in equal quantities. pH of mixture was maintained at 8.2 by using freshly prepared NaOH solution. Then solution is refluxed for about 5hrs. and kept undisturbed for 7days. After 7 days, brown colored precipitate was obtained. The product is filtered, dried and weighed. The yield of product is approximately 25.7%.

3. Results and Discussions :

For the determination of stability constants, Turner and Anderson's Modified Job's Method were used.

Suppose the initial concentration of metal ions are 'a' and that of ligands 'b' then the stability constant 'K' is given by

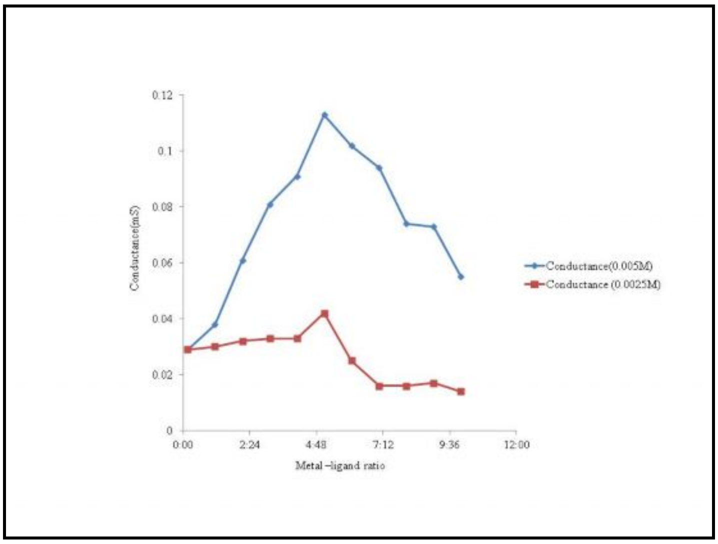
$$K = \frac{x}{(a-x)(b-x)} \quad \text{-------------- (II)}$$

Where 'x' is the concentration of complex.

From the intercept on the two curves at same conductance, the stability constant was calculated i.e. a_1, a_2 and b_1, b_2 represent the concentration of metal and ligand respectively for 1:1 complex. Hence equation (II) became

$$\frac{(a2-a1)}{(a1-x)} = \frac{(b1-b2)}{(b2-x)} \quad \text{------------- (III)}$$

Log K values are determined from (**Graph II)**



Graph II :Conductometric estimation of composition of complex of 1-Benzothiazol-2-yl-3-(2-hydroxy phenyl)-5-(4-chlorophenyl) pyrazoline (L^3) and $Co(NO_3)_2.6H_2O$

For the other ligand solutions L^1,L^2,L^3,L^4,L^5 & L^6 with Co(II), Ni(II),Cu(II) log K values are given in (**Table III)**

Table III : Comparative log K values of stability constants of complexes Co(II), Ni(II), Cu(II) with ligand L^1 to L^6

S.N.	System	Conductometric	pH-metric
1	Co(II)-L^1	2.50	2.45
2	Ni(II)-L^1	1.99	1.96
3	Cu(II)-L^1	1.83	1.3
4	Co(II)-L^2	1.67	1.7
5	Ni(II)-L^2	1.70	1.69
6	Cu(II)-L^2	1.72	1.78
7	Co(II)-L^3	2.20	2.19

8	Ni(II)-L^3	1.89	1.62
9	Cu(II)-L^3	2.03	2.09
10	Co(II)-L^4	1.98	1.99
11	Ni(II)-L^4	1.86	1.81
12	Cu(II)-L^4	1.55	1.54
13	Co(II)-L^5	1.90	1.91
14	Ni(II)-L^5	1.63	1.66
15	Cu(II)-L^5	1.46	1.43
16	Co(II)-L^6	1.58	1.59
17	Ni(II)-L^6	1.76	1.76
18	Cu(II)-L^6	1.58	1.53

The stability constant was determined by pH-metry also. The stability constants of the complexes implemented for the study are presented in table[35]. The values determined by both techniques reflects the confirm formation of complex between metal ion and ligand.

3.1 Determination of Thermodynamic Paramaters :

Stability of complex depends on reaction energy i.e. thermodynamic stability is concerned with metal-ligand bond energies and stability constants.

On the basis of log K values, free energy change of the system can be calculated by using following equations

$\Delta G = -2.303\ RT \log K$ --------------- (IV)

Where, R = Gas constant & T = absolute temperature.

The free energy change can also be calculated on the basis of pH-metry. Hence the comparative values are shown in (**Table IV).**

Table IV : Comparative values of ΔG ($JK^{-1}mol^{-1}$) of ligands L^1 to L^6 with Co(II), Ni(II), Cu(II)

S.N	Systems	Conductometry	pH-metry
1	L^1+Co(II)	-14408.74	-14214.39
2	L^2+Co(II)	-9625.04	-9863.04
3	L^3+Co(II)	-12679.69	-12705.92
4	L^4+Co(II)	-11411.72	-11545.56
5	L^5+Co(II)	-10950.64	-11081.42
6	L^6+Co(II)	-9106.32	-9224.85
7	L^1+Ni(II)	-11469.36	-11371.51
8	L^2+Ni(II)	-9797.94	-9805.03
9	L^3+Ni(II)	-10893.01	-9398.90
10	L^4+Ni(II)	-10720.10	-10501.24
11	L^5+Ni(II)	-9394.50	-9630.97
12	L^6+Ni(II)	-10143.75	-10211.15
13	L^1+Cu(II)	-10547.20	-7542.33
14	L^2+Cu(II)	-9913.21	-10327.19
15	L^3+Cu(II)	-11699.90	-12125.74
16	L^4+Cu(II)	-8933.42	-8934.76
17	L^5+Cu(II)	-8414.70	-8296.56
18	L^6+Cu(II)	-9106.32	-8876.74

On the basis of all these data, it has been observed that the formation constant or formation of complex of N- benzothiazole-2-yl-3,5- disubstituted pyrazoline with Co(II), Ni(II), Cu(II) takes place in 1:1 ratio. Hence it is proved that, the Modified Job's Method of continuous variation was used to calculate stability constants and free energy change.

During the complexometric titration, complex formation was confirmed by the formation of precipitate during titration and change in the color of solution. This happened due to the formation of 1:1 complex by replaceable H^+ from the phenolic –OH group.

While in the values of formation constants some variations are obtained, it may be due to

a) Abnormal conductance of hydrogen and hydroxyl ions[36].

The size of hydrogen ion in solution is very small and because of its effective size and conducting power it combine with the water molecule forming H_3O^+ ion. While the conductance of hydroxyl ion in water is less than that of hydrogen ion and hence behave abnormally.

b) Differ in size of metals :

Typically the chemistry of transition metal complexes is dominated by interactions between s and p molecular orbital's of the ligands and the orbital's of the metal ions. The s,p and d orbital's of the metal can accommodate 18 e^-s. The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion and to the ratio of the size of ligands and metal ion. Large metals and small ligands lead to high coordination number. Small metals with large ligands leads to low coordination number. Due to their large size early transition metals tend to have high coordination number.

c) The conductivity of an ionic solution increases with increasing concentration. In strong electrolytes conductivity increases and in weak electrolytes it is more gradual. This is so happened because of increase in the number of ions per unit volume of the solution.

d) The effect of temperature and pressure is also takes place on conductivity. The increase in temperature and pressure, the conductance of the solution increases.

So because of all these factors variations may be obtained in the results.

The negative values of free energy shows that the formation of complex is feasible and spontaneous.

5. Conclusion :

On the basis overall information N-Benzothiazol-2-yl-3,5-disubstituted pyrazoline with transition metals shows 1:1 complex formation.

Complex formation reaction involves changes in the number of ions then there would be changes in conductivity of solution. In the complexation reaction there is a decrease in number of ions in solution. Hence the conductance of solution decreases due to formation of complex. Similarly, if the complex formation involves the liberation or absorption of protons or hydroxyl ions, then the conductance of the solution changes abnormally. This is because of the abnormal conductivity of the protons and hydroxyl ions in aqueous solutions. This change in conductance can be used to detect the complex formation[37].

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