Stoichiometric Studies on formation of Azomethine-Cu(II), Co(II) and Fe(III) Complexes

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Abstract: Stability Constant and Free energy change during the formation of complexes of azomethine derivative with Cu (II), Co(II) & Fe(III) have been determined by absorbance measurement using mole ratio method. Complexes of azomethine derivative were prepared by adding acetonic solution of chlorides of Cu(II), Co(II) and Fe(III) to the solution of Ligand i.e. azomethine derivative. Change in colour was observed when solutions of the above mentioned metal chlorides were added to solution of chelating agent. It has been found from the study that one mole of azomethine derivative reacts with one mole of each Cu(II) and Co(II), while two moles of azomethine derivative react with one mole of Fe(III) to form stable complex.

Key Words: Complexation, Azomethine, Stability Constant, Free Energy Change, Mole Ratio Method.

Introduction

Complexation of most chelating agents is possible with most of the metals present in periodic table. Several investigations for complexation have been performed for metals of transition series. The chemistry of metal complexes involves the reaction of metals with coordinating and chelating agents having Nitrogen, Oxygen, Sulphur and Phosphorus etc.; which serve as electron donating species and donate loan pair(s) of electrons to the metals. Therefore, there exists enough scope to investigate complexation or chelating behavior of some newly prepared chelating agents. These chelating agents may be azomethine, because these have nitrogen as electron donor atom.

Stability constant determination is very essential for a proper understanding of system involving complexation / chelation. Knowledge of stability constant also helps in calculation of various thermodynamic constants. Numbers of methods are available for the calculation of stability constant of the complexes, using absorbance measurement.

Lewis & Rendell[1] introduced the concept of ionic strength which later received theoretical justification from the Debye-Huckel theory[2]. The classical approach for the evaluation of thermodynamic constants involves the determination of stability constant in the ratio of different ionic strength followed by extrapolation to zero ionic strength (infinite dilution). Some workers[3] used the value of a single determination and attempted to correct this value to a thermodynamic equilibrium constant by the application of Debye-Huckel theory.

Another method was introduced by Siecermann and Silien[4], and the fundamental idea of this method is to control the activity coefficient by keeping ionic strength constant, because, in very dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of identical ionic strength. During the present study, the ionic strength could nt be kept constant as the investigations are carried out in purely non aqueous media and it is observed that even trace of moisture would decompose the complex and even mixed solvents containing water and organic solvents could not be used. The stability constant data incorporated in this study refer to arbitrary values only.
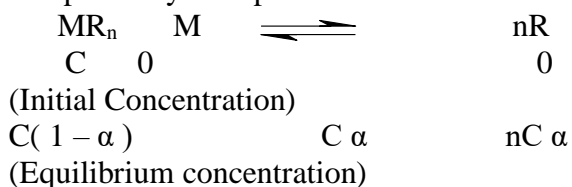
The stability constant can be determined experimentally by the method described in early 20th century[5-6]. Later on the work of Bjerrum[7] played an outstanding role in this reference. The pH-metric method of determining the equilibrium concentrations of ligands and calculating formation function developed by Bjerrum[8] is also very important. Almost half of the stability constants of the chelates and other coordination compounds have been extensively carried out by this method[9]. Current interest about the formation of stability of metal ion complexes in solution has been indicated in number of reviews[10-14].

The main objective of the study is to know the nature of complexes of azomethine with Cu, Co and Fe. Study is based on the classical methods which are used to evaluate stability constant and free energy change during the chelation.

Methodology

Initially, complexes of ligand (azomethine) were prepared by adding chlorides of Cu, Co and Fe(III). Colour change was observed when acetonic solutions of the above metal salts were added to chelating agent. The stability constant and free energy change during complexation have been calculated using Mole ratio method[15-16]. This method is based on absorbance measurement[17]. Method is as follows:

If the complex contains metal ion M and reagent R in the ratio 1:n, the dissociation of the complex may be represented as

$$MR_n \rightleftharpoons M + nR$$

C	0	0

(Initial Concentration)

$$C(1-\alpha) \qquad C\alpha \qquad nC\alpha$$

(Equilibrium concentration)

where, C is the total concentration of the complex in moles per liter assuming no dissociation, α is the degree of dissociation. Then stability constant may be expressed as

$$K = \frac{C(1-\alpha)}{\alpha C . (n\alpha C)^n} \qquad (1)$$

The value of n for the complex having been established, the value of α may be obtained from the mole-ratio curves by the following relationship

$$\alpha = \frac{E_m - E_s}{E_m} \qquad (2)$$

Where, E_m is the maximum extinction in presence of large excess of the reagent, obtained from the horizontal portion of the curve, indicating that all the metal is bound in complex and E_s is the extinction at the Stoichiometric ratio of the ligand to the metal in complex, the total concentration of the complex being the total concentration of metal. When both the reactants are colorless the curve generally breaks abruptly at the Stoichiometric ratio and α is not reliable in such cases.

In a system, when the combining ratio of metal:chelating agent is 1:1, the above equation (1) reduces to

$$K = \frac{C(1-\alpha)}{\alpha C . \alpha C} = \frac{1-\alpha}{C\alpha^2}$$

and for a system where the combining ratio of metal:complexing agent is 1:2, equation (1) takes the form:

$$K = \frac{C(1-\alpha)}{(2\alpha C)^2} = \frac{1-\alpha}{4\alpha^3 C^2} \alpha C .$$

The value of α may be obtained from the equation (2). Where "K" is stability Constant.

Change in free energy is calculated by $\Delta f^0 = RT \ln K$

Observations and Results

Table.1: Absorbance measurement for Cu-complex

Set – I: Strength of Ligand solution: 1.25×10^{-3} M

Set – II: Strength of Ligand solution : 1.0×10^{-3} M

Volume of $CuCl_2$ solution : 1.0 ml.

Total Volume : 10.0 ml (For both sets)

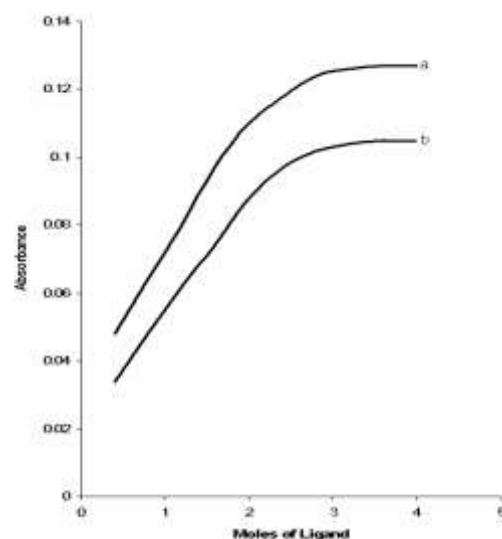| Set – I (Curve a)		Set – II (Curve b)	
Volume of Ligand solution	Absorbance	Volume of Ligand solution	Absorbance
0.40	0.048	0.40	0.034
0.80	0.064	0.80	0.048
1.20	0.08	1.20	0.062
1.60	0.097	1.60	0.074
2.00	0.11	2.00	0.088
2.40	0.118	2.40	0.097
2.80	0.124	2.80	0.102
3.20	0.126	3.20	0.104
3.60	0.127	3.60	0.105
4.00	0.127	4.00	0.105

Fig.1: Composition of Cu-complex by Mole-ratio Method

From the above data:

E_m = 0.127

E_s = 0.118

Then,

$$\alpha = \frac{0.127 - 0.118}{0.127}$$

= 0.071

Substituting the value of C and α in equation

$$K = \frac{1 - 0.071}{(0.0001) \times (0.071)^2}$$

= 1.843×10^6

Change in free energy is calculated by

$-\Delta f^0$ = RT ln K

= 1.987 x 303 x 2.303 Log K

= 1.987 x 303 x 2.303 Log (1.843×10^6)

= 7.79 K Cal / Mole.

Table.2: Absorbance measurement for Co-complex

Set – I: Strength of Ligand solution: 1.25×10^{-3} M

Set – II: Strength of Ligand solution: 1.0×10^{-3} M

Volume of CoCl$_2$ solution : 1.0 ml.

Total Volume : 10.0 ml (For both sets)

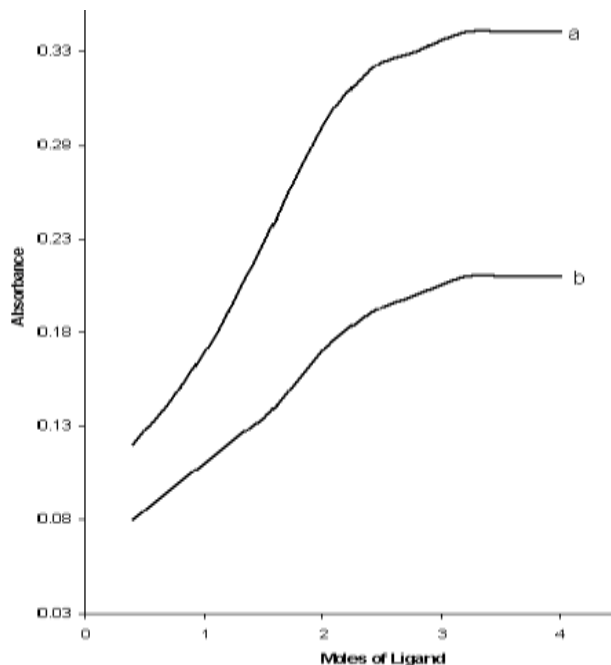| Set – I (Curve a)		Set – II (Curve b)	
Volume of Ligand	Absorbance	Volume of Ligand	Absorbance
0.40	0.12	0.40	0.08
0.80	0.15	0.80	0.1
1.20	0.19	1.20	0.12
1.60	0.24	1.60	0.14
2.00	0.29	2.00	0.17
2.40	0.32	2.40	0.19
2.80	0.33	2.80	0.2
3.20	0.34	3.20	0.21
3.60	0.34	3.60	0.21
4.00	0.34	4.00	0.21

Fig.2: Composition of Co-complex by Mole-ratio Method

From the mole ratio curve

E_m = 0.34
E_s = 0.32

Then

$$\alpha = \frac{0.34 - 0.32}{0.32}$$

= 0.0588

Substituting the value of C and α in equation

$$K = \frac{1 - 0.0588}{(0.0001) \times (0.0588)^2}$$

= 2.723×10^6

Change in free energy is calculated by

$-\Delta f^0$ = RT ln K

= 1.987 x 303 x 2.303 Log K

= 1.987 x 303 x 2.303 Log (2.723×10^6) = 7.72 K Cal / Mole.

3

Table.3: Absorbance measurement for Fe-complex

Set – I: Strength of Ligand solution: 1.25×10^{-3} M

Set – II: Strength of Ligand solution: 1.0×10^{-3} M

Volume of $FeCl_3$ solution   :   1.0 ml.

Total Volume   :   10.0 ml (For both sets)

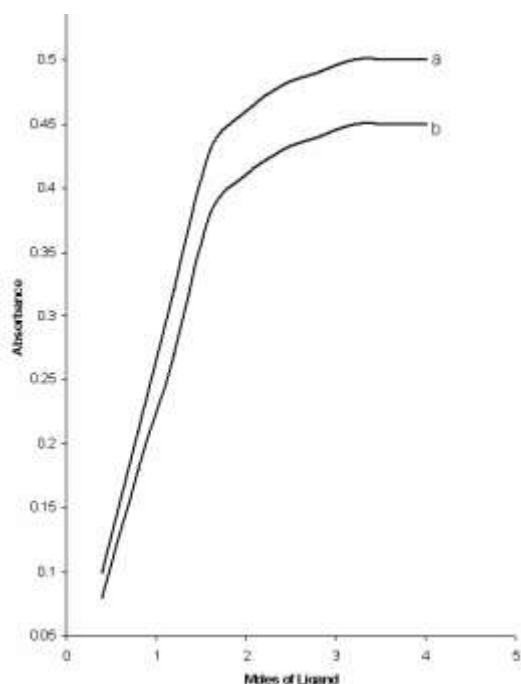| Set – I (Curve a)		Set – II (Curve b)	
Volume of Ligand Solution	Absorbance	Volume of Ligand Solution	Absorbance
0.40	0.1	0.40	0.08
0.80	0.21	0.80	0.18
1.20	0.32	1.20	0.27
1.60	0.43	1.60	0.38
2.00	0.46	2.00	0.41
2.40	0.48	2.40	0.43
2.80	0.49	2.80	0.44
3.20	0.5	3.20	0.45
3.60	0.5	3.60	0.45
4.00	0.5	4.00	0.45

Fig. 3: Composition of complex by Mole-ratio Method

From the mole ratio curve

E_m = 0.50
E_s = 0.43

Then,

$$\alpha = \frac{0.50 - 0.43}{0.50}$$

= 0.14

Substituting the value of C and α in equation (1)

$$K = \frac{1 - 0.14}{4 \times (0.0001)^2 \times (0.14)^3}$$

= 0.7818×10^{10}

Change in free energy is calculated by

$-\Delta f^0$ = RT ln K

= $1.987 \times 303 \times 2.303$ Log K

= $1.987 \times 303 \times 2.303$ Log (0.7818×10^{10})

= 13.78 K Cal / Mole.

Conclusion

The stability constant of the complex was found to be 1.843×10^6 and the free energy change at 30^0C was 7.79 KCal / mole in case of Cu(II) complex and 2.723×10^6 and 7.72 KCal / mole respectively in case of Co(II) complex; while 0.7818×10^{10} and 13.78 KCal / mole respectively in case of Fe(III) complex. It has been Obtained from the study that one mole of azomethine derivative reacts with one mole of each Cu(II) and Co(II), while two moles of azomethine derivative react with one mole of Fe(III) to form stable complex. This result is very much similar to the findings of other researchers[17-18]. Figure A, B and C represent structures of chelating agent with Cu(II), Co(II) and Fe(III) respectively.
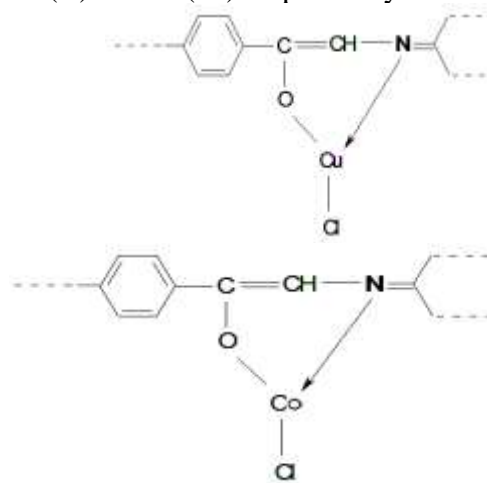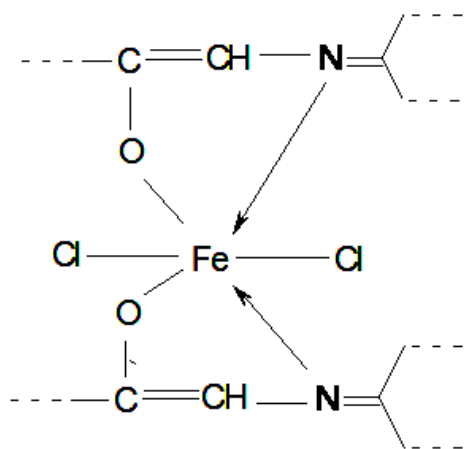

Fig. – 4

Fig. - 5

As colour change was observed during formation of complexes, these azomethine may be used to detect metals qualitatively and quantitatively in different type of samples. Complexes may be used as coloring agents in different processes.

References

1. Lewis, G. N. & Rendell, M. *J. Am. Chem. Soc.*, 43: 1112 (1921).
2. Whittaker, A. G., Mount, A. R. & Heal, M. R. "Physical Chemistry" 1st Ed., BS Pub. Ltd., Oxford (2001).
3. Izatt, R. M., Mess, G. G., Block, B. P. Ferrilius, W. C. *J. Am. Chem. Soc.*, 58: 1133 (1954).
4. Sierermann, G. & Silies, L. G. *Arkiv. Kemi.*, 05: 425 (1953).
5. Bodlender, G. & Fitting, R. *Z. Phys. Chem.* 34: 57 (1902).
6. Morze, H. *Phys. Chem.* 41: 709 (1907).
7. Bjerrum, N. *Kgl.Denske. Videnskab. Seshela.*, 21: 4 (1944).
8. Bjerrum, J. *Chem. Rev.*, 46: 381 (1950).
9. Schwarrenback, G. *Helv. Chim. Acta.*, 82: 899 (1949).
10. Anonyms, "Discussion on co-ordination chemistry" I.C.I. Report, BRL / 105, Walwyn (1950).
11. Burkin, A. R. *Quert. Rev. Chem. Soc.*, 5:1 (1951).
12. Martell, A. E. & Calvin, M. "Chemistry of Metal Chelate Compounds" Prentice Hall, New York (1952).
13. Calvin, M. "Chelation and Catalysis" W. D. McLomy & B. Gloss.
14. Mertell, A. E. *Annl. Rev. Phy. Chem.,* 6: 239 (1955).
15. Yoe, J. H. & Harvey, A. E. *J. Am. Chem. Soc.,* 78: 668 (1948).
16. Yoe, J. H. & Jones, A. L. *Ind. Eng. Chem. Anal.,* 16: 111 (1944).
17. Gupta, A. K. "D. Phil. Thesis", submitted to Garhwal University, Srinagar Garhwal (India). (1980).
18. Rathee, N. S. "Thermodynamic Studies on Azomethine - Cd (II) and Mn(II) Chelation" *Int. J. Phy., Chem, Math Sc.,* 05(02): 01-04 (2016).