Garima, 2025, 13:1
ISSN (Online): 2348-4098
ISSN (Print): 2395-4752

International Journal of Science, Engineering and Technology
An Open Access Journal

Thermodynamic Studies on New Schiff Base - Cu(II) and Ni(II) Chelation

Garima[1], Ravi Kumar Rana[1], Niranjan Singh Rathee[2]
[1]Department of Chemistry, Baba Mastnath University, Rohtak (Haryana)-124001, India
[2]Department of Science, Jagannath University, Bahadurgarh, Jhajjar (Haryana) -124507, India

Abstract- A Schiff base ligand, 2,2′- ((1E,1′E)- ((4-methyl-1,3-phenylene) bis(azanylylidene)) bis (methanylylidene) bis(4-bromophenol), was synthesized via a condensation reaction between 5-bromosalicylaldehyde and 4-methyl-1,3-phenylenediamine. The synthesized ligand was subsequently used to prepare Ni(II) and Cu(II) metal complexes. The stability constants and free energy changes associated with the chelation of the Schiff base ligand with Cu(II) and Ni(II) ions were determined using UV–visible absorbance measurements employing the mole ratio method. The results indicated that one mole of the Schiff base ligand coordinates with one mole of each metal ion, forming stable 1:1 metal–ligand chelates. These results obtained from calculation of Stability Constant and Free Energy Change during chelation demonstrates that the Cu(II) chelate is thermodynamically more stable than the Ni(II) chelate under the studied conditions.

Keywords: Schiff Bases, Complexes, Stability Constant and Free Energy Change.

I. INTRODUCTION

Chelation is possible with most of the metals present in the periodic table; however, the majority of investigations have been focused on transition metal ions. The chemistry of metal complexes involves reactions between metal ions and coordinating or chelating agents containing donor atoms such as nitrogen, oxygen, sulfur, and phosphorus, which act as electron donors to the metal center. Consequently, there is considerable scope for investigating the stoichiometry and stability of new chelates, particularly those that may exhibit selectivity toward transition and non-transition metals.

Among chelating agents, Schiff bases have attracted significant attention due to the presence of azomethine nitrogen donor atoms, which readily participate in metal coordination. Determination of the stability constant is essential for a proper understanding of chelation systems, as thermodynamic parameters such as the free energy change can be derived directly from these constants. Several experimental methods have been developed for the determination of stability constants of metal complexes using absorbance measurements in both aqueous and non-aqueous media. Broadly, two main approaches are commonly employed. Lewis and Randall [1] introduced the concept of ionic strength, which later received theoretical justification through the Debye–Hückel theory [2]. The classical method for evaluating thermodynamic constants involves determining stability constants at different ionic strengths, followed by extrapolation to zero ionic strength (infinite dilution). Some researchers [3] have attempted to obtain thermodynamic equilibrium constants from a single determination by applying corrections based on the Debye–Hückel theory.

The second approach, proposed by Sillén and Siegbahn [4], is based on maintaining a constant ionic strength so as to control activity coefficients. In very dilute solutions, the activity coefficient of a given strong electrolyte remains constant in all solutions of identical ionic strength. However, in the present study, maintaining constant ionic strength was not feasible because the investigations were carried out in purely non-aqueous media. It was observed that even trace amounts of moisture led to decomposition of the complexes, and mixed solvents containing water could not be employed. Therefore, the stability constant values reported in this study represent arbitrary values rather than true thermodynamic constants.

The experimental determination of stability constants can be carried out using several techniques. Early methods were reported in the early twentieth century [5–6], followed by the seminal contributions of Bjerrum [7], which significantly advanced the field. The concept of stepwise complex formation, developed through the work of Babko in the U.S.S.R. [8], further enhanced the understanding of metal–ligand equilibria. Bjerrum's pH-metric method, involving the determination of equilibrium ligand concentrations and the calculation of formation functions [9], has proven particularly important. Nearly half of the reported stability constants of chelates and coordination compounds have been determined using this technique [10]. Ongoing interest in the formation and stability of metal ion complexes in solution is reflected in numerous comprehensive reviews [11–15].

II. METHODOLOGY

Initially, complexes of the ligand (Schiff base) were prepared by reacting it with Cu(II) chloride and Ni(II) chloride. A distinct color change was observed upon the addition of acetonic solutions of these metal salts to the chelating agent, indicating complex formation. The stability constants and free energy changes associated with the chelation process were calculated using the mole ratio method [16–17], which is based on UV–visible absorbance measurements [18].

If the complex formed contains a metal ion M and reagent R in the stoichiometric ratio 1 : n, the stability constant (K) may be expressed as:

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

Once the value of n for the complex has been established, the value of α (the degree of dissociation of the complex) can be obtained from the mole-ratio curves using the following relationship:

$$\alpha = \frac{Em - Es}{Em} \qquad (2)$$

Where E_mis the maximum absorbance (extinction) observed in the presence of a large excess of the reagent, obtained from the horizontal portion of the mole-ratio curve, indicating that all the metal ions are bound in the complex, and E_sis the absorbance at the stoichiometric ligand-to-metal ratio in the complex. The total concentration of the complex is assumed to be equal to the total concentration of the metal ion. When both reactants are colorless, the mole-ratio curve generally exhibits an abrupt break at the stoichiometric ratio, and under such conditions the calculated value of α is not reliable.

For a system in which the combining ratio of metal to chelating agent is 1:1, equation (1) reduces to:

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

For a system in which the combining ratio of metal to complexing agent is 1:2, equation (1) takes the form:

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

The value of α may be obtained from the equation (2).

Change in free energy is calculated by - Δf0 = RT In K (Where K is stability Constant).

Results

The color change observed upon mixing the azomethine derivative with Cu(II) chloride and Ni(II) chloride was light yellow and light brown, respectively, indicating the formation of metal–ligand complexes. The absorbance measurements obtained using the mole ratio method are tabulated below:

Set – I: Strength of Schiff Base solution = 1.25 x 10-3 M

Set – II: Strength of Schiff Base solution = 1.0 x 10-3 M

Volume of Cu(II / Ni(II) Chloride solution = 1.0 ml.

Total Volume = 10.0 ml (For both sets)

Schiff Base – Cu(II) Complex Schiff Base – Ni(II) Complex

Set – I Set – II Set – I Set – II

Volume of Schiff Base Solution (ml) Absorbance Volume of Schiff Base

Solution (ml) Absorbance Volume of Schiff Base Solution (ml) Absorbance Volume of

Schiff Base – Cu(II) Complex				Schiff Base – Ni(II) Complex			
Set – I		Set – II		Set – I		Set – II	
Volume of Schiff Base Solution (ml)	Absorbance	Volume of Schiff Base Solution (ml)	Absorbance	Volume of Schiff Base Solution (ml)	Absorbance	Volume of Schiff Base Solution (ml)	Absorbance
0.4	0.11	0.4	0.7	0.4	0.10	0.4	0.6
0.8	0.14	0.8	0.10	0.8	0.13	0.8	0.9
1.2	0.19	1.2	0.13	1.2	0.18	1.2	0.12
1.6	0.20	1.6	0.16	1.6	0.21	1.6	0.15
2.0	0.23	2.0	0.19	2.0	0.23	2.0	0.18
2.4	0.26	2.4	0.22	2.4	0.25	2.4	0.21
2.8	0.28	2.8	0.25	2.8	0.27	2.8	0.24
3.2	0.30	3.2	0.26	3.2	0.29	3.2	0.25
3.6	0.31	3.6	0.27	3.6	0.30	3.6	0.26
4.0	0.31	4.0	0.27	4.0	0.30	4.0	0.26

Stability Constant and Free Energy Change in Schiff Base-Cu(II) Chelation

Stability Constant

Fron the above table, Em = 0.30 and Es = 0.26

Then,

$$\alpha = \frac{0.30 - 0.26}{0.30} = 0.1333$$

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

$$K = \frac{1 - 0.1333}{(0.0001) \times (0.1333)^2} = 0.488 \times 10^6$$

Change in free energy is calculated by

- Δf0 = RT ln K

= 1.987 x 303 x 2.303 Log K

= 1.987 x 303 x 2.303 Log (0.488 x 106)

= 7.887 KCal / Mole.

Stability Constant and Free Energy Change in Schiff Base-Ni(II) Chelation

Stability Constant

Fron the above table, Em = 0.29 and Es = 0.25

Then,

$$\alpha = \frac{0.29 - 0.25}{0.29} = 0.1379$$

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

$$K = \frac{1 - 0.1379}{(0.0001) \times (0.1379)^2} = 0.478 \times 10^6$$

Change in free energy is calculated by

- Δf0 = RT ln K

= 1.987 x 303 x 2.303 Log K

= 1.987 x 303 x 2.303 Log (0.478 x 106)

= 7.874 KCal / Mole.

III. CONCLUSION

The experimental results clearly demonstrate that the synthesized Schiff base ligand forms stable 1:1 chelates with both Cu(II) and Ni(II) ions, as confirmed by the mole ratio method using absorbance measurements. The observed color changes upon complexation further support the formation of metal–ligand complexes. The calculated stability constants indicate that the Cu(II) complex (0.488 x 106) is thermodynamically more stable than the Ni(II) complex (0.478 x 106). This difference in stability may be attributed to variations in ionic size, electronic configuration, and metal–ligand bonding characteristics. The corresponding free energy changes at 300 K, name 7.887 kcal mol^{-1} for Cu(II) chelate and 7.874 kcal mol^{-1} for Ni(II) chelate, further confirm the spontaneous nature of the chelation process. These findings are consistent with previously reported studies on Schiff base metal complexes [18-20], validating the reliability of the experimental approach and highlighting the potential of Schiff Base ligands for forming stable coordination compounds with divalent metal ions.

Future Scope

New Schiff Bases derivatives and their complexes with various metal ions may be prepared and some biological and analytical applications of the same may be evolved.

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