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Stability constants of complexes of bromobenzoylthioacetophenone and their medicinal significance

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Abstract- Our body produces and consumes many complexes during various physiological processes. Metal complexes work as drugs and chemotherapeutic agents. Complexes of p-bromobenzoylthioacetophenone, an organic ligand have been found to possess therapeutic values. Complexation of this ligand was made with bivalent transition metals namely Copper, Nickel, Zinc and Cadmium. Stability constants of these complex have been determined potentiometrically using Calvin-Bjerrum technique. The order of stability of these complexes along with their medicinal significance has been discussed

Key words: Stability constant, Solution equilibria, Medicinal Significance

INTRODUCTION

Para-bromobenzoylthioacetophenone, the ligand chosen for the present research work belongs to Monothio- β -diketone family.¹⁻³ This organic ligand itself having good therapeutic value behaves as uninegatively charged bidentate (O, S) chelating agent forming a six-membered chelate⁴ with metal ions. It deprotonates through enol or enethiol form.⁵⁻⁷

A number of complexes of Monothio- β -diketone with different nature have been reported with their curative measures. The structure of the ligand chosen for the present work is shown below.

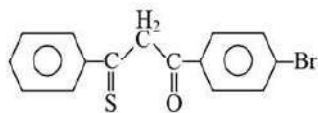


Fig. 1- p-bromobenzoylthioacetophenone

No attempt however has been made so far to study the solution equilibria of this ligand and its derived metal complexes as also the medicinal aspects of these complexes which can help to understand the effect of bromine substituent on the stability constants of the complexes. The stability constant has great say in the therapeutic values of the complexes.

In this communication, we report the Stability Constants⁸⁻¹⁰ of the complexes of p-bromobenzoylthioacetophenone with Copper, Nickel, Zinc and Cadmium at three different temperatures at a fixed ionic strength of 0.1 M KCl as determined by Calvin-Bjerrum¹¹⁻¹³ and modified by Irving and Rossotti.^{13,14}

Experimental

By the reported method, the said ligand was synthesised by Claisen condensation as shown below.

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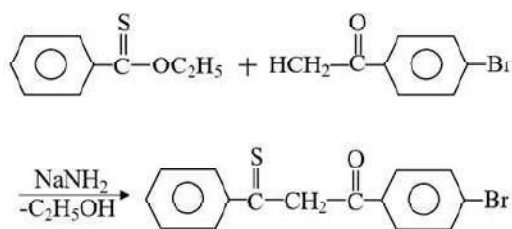


Fig. 2- Synthesis of p-bromobenzoylthioacetophenone

Following three mixtures were prepared for potentiometric titration.

- (i) Mixture (i): 5 ml 0.4 M HCl solⁿ + 5 ml M KCl solⁿ
- (ii) Mixture (ii): Mixture (i) + 5 ml 0.02 M Ligand solution
- (iii) Mixture (iii): Mixture (ii) + 5ml 0.004 M Metal ion solution

Standard solution of ligand was prepared in dioxan.^{15,16}

Total volume was kept 50 ml in each case. The mixtures were titrated against 0.2 M KOH solution and the pH was measured in Oxygen-free nitrogen atmosphere. The pH-meter readings (B values) and the volume of alkali when plotted against each other provided Acid, Ligand and Complex Titration Curves respectively.

Similar graphs were obtained at 20°C and 30°C.

Values of \bar{n}_A obtained from acid and ligand titration curves to find the pKa (Protonation constant) value of ligand. Values of \bar{n} and pL were obtained by plotting \bar{n} versus pL to get stepwise stability constant of the complexes. These values are furnished below.

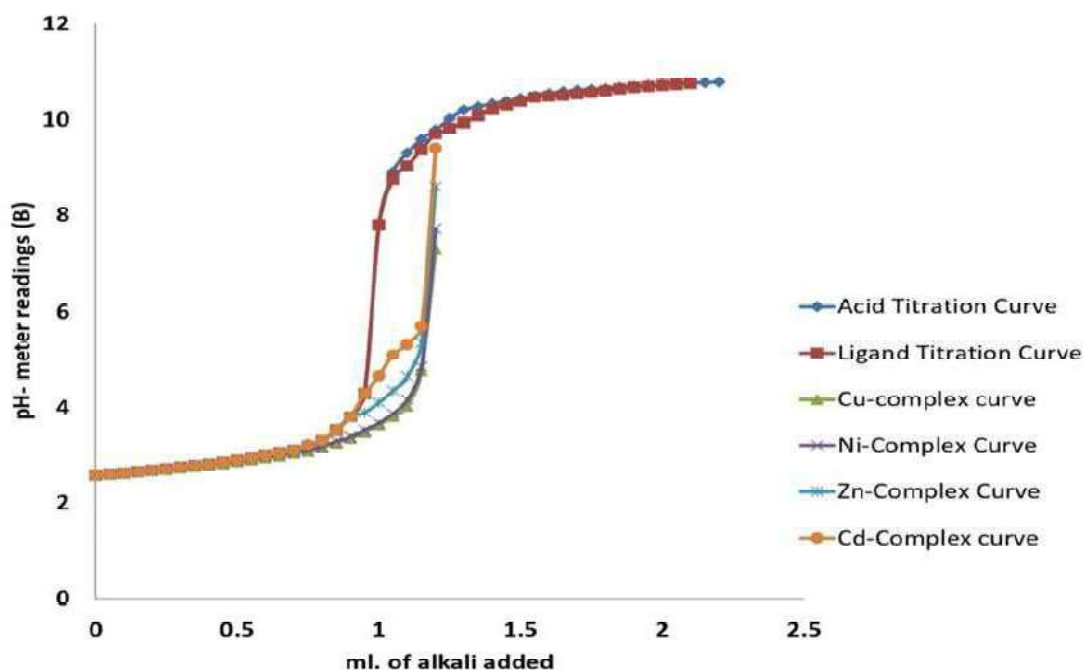


Fig. 3- Ligand & Metal-Complex Titration Curves at 10°C

Table 1- Stepwise and Overall Stability Constant Data of Metal Complexes at three different temperatures [Medium = 75% aq. Dioxan(v/v); $\mu = 0.1$ M KCl]

Metal Ions	Temperatures								
	10°C			20°C			30°C		
	Log K ₁	Log K ₂	Log β	Log K ₁	Log K ₂	Log β	Log K ₁	Log K ₂	Log β
Cu ²⁺	10.69	09.84	20.53	10.55	09.73	20.28	10.47	09.68	20.15
Ni ²⁺	10.65	09.65	20.30	10.44	09.54	19.94	10.36	09.47	19.83
Zn ²⁺	09.75	08.97	18.72	08.93	08.43	17.36	08.87	08.39	17.26
Cd ²⁺	08.99	08.44	17.43	08.88	08.31	17.19	08.72	08.18	16.90

RESULTS & DISCUSSION

From the table above, it is obvious that the Stability order of metal complexes follow the trend: Cu(II) > Ni(II) > Zn(II) > Cd(II). It is obvious that Overall Stability Constants of all the metal complexes are greater at lower temperature. The above trend is in conformity with the stability order reported for the complexes of these metals with several other monothio- β -diketones studied so far.

A comparison of the stability data of the present investigation with stability data of the previous work with parent monothio- β -diketone reveals that the overall stability constants of all the four metal complexes in the present investigation at 30°C are less than those of the respective complexes derived from Benzoylthioacetophenone, the parent ligand. This reflects that the substitution by Bromine at para position of the benzoyl ring in the ligand decreases the stability of the derived metal complexes. This decrease in the stability of the complexes may be probably due to steric hindrance caused by bromine substituent. It may also be due to increased acidic strength of ligand as is obvious from its protonation constant ($\text{Log } K_1^H$) values compared to its parent compound. Thus, in comparison to its parent compound, the complexes of the ligand in question have intensive curative values.

CONCLUSION

While the ligand has a weak tendency to deprotonate, it had a very strong tendency to coordinate the metal ions. This fact is substantiated by very low dissociation constants of the ligand and very high stability constants of its complexes.

All these complexes are chelates and chelated transition metal ions have been found in a variety of biochemical situations. Complexes of Copper, Cobalt and Zinc with this ligand have been found very useful to prevent and cure pernicious anaemia.

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REFERENCES

1. **Chaston S. H. H. & Livingstone S. E. 1964.** Thio-derivatives of beta-diketones. *Proceedings of the Chemical Society of London.* 111
2. **Livingstone S. E. 1971.** Monothio- β -diketones and their metal complexes. *Coord. Chem. Rev.* **7:** 59-80
3. **Livingstone S. E. 1965.** Metal complexes of ligands containing sulphur, selenium, or tellurium as donor atoms. *Quart. Rev. Chem. Soc.* **19:** 420-421
4. **Belcher R., Stephen W. I., Thomson I. J. & Uden P. C. 1971.** Volatile metal chelates of monothio acetylacetone. *J. Inorg. and Nucl. Chem.* **33:** 1852
5. **Berg U., Sandström J., Carlsen L. & Duus F. 1983.** β -Thioxoketones. Part 9. A dynamic ^1H nuclear magnetic resonance spectroscopic study of thioacetylacetone and related β -thioxoketones. Direct observation of the enol and enethiol tautomeric constituents and their interconversion. *J. Chem. Soc., Perkin Transactions.* **2(9):** 1321-1322
6. **Joergensen F. S., Brown, R. S., Carlsen, L. & Duus, F. 1982.** X-ray photoelectron spectroscopic study of the enol-enethiol tautomerism of thioacetylacetone and related β -thioxoketones. *J. Am. Chem. Soc.* **104(22):** 5922
7. **Dubey B. R., Bansal R. K. & Rai A. K. 1988.** ^{13}C & ^{19}F NMR studies of para-substituted monothio- β -diketones & their Zn (II) Complexes. *Indian Journal of Chemistry.* **27:** 256
8. **Keemti L. & Malhotra S. R. 1981.** Stepwise stability constants of some bivalent metal ion complexes with 3-bromo-2-hydroxy-5-methylacetophenone, its oxime and hydrazone. *South African Journal of Science.* **77:** 238
9. **Singh J., Srivastav A. N., Singh N. & Singh A. E., 2019.** Stability constants of metal complexes in solution. *Stability and applications of coordination compounds.* **Chapter 3:** 3-5
10. **Athawale V. & Nerkar S. 2000.** Stability constants of complexes of divalent and rare earth metals with substituted salicylnals. *Monatshefte für Chemie.* **131:** 269-270
11. **Vartak D. G. & Menon N. G. 1966.** Vartak, D. G., and N. G. Menon. Solution stability constants of complexes of 4-nitro-2-aminophenol with some divalent metal ions. *J. Inorg. and Nucl. Chem.* **28:** 2912-2916

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12. **Bjerrum J. 1941.** Metal amine formation in aqueous solution. Haase, Copenhagen
13. **Calvin M. & K. W. Wilson.1945.** Stability of chelate compounds. *J. Am. Chem. Soc.* **67**: 2003
14. **Irving H. M. & Rossotti H. S. 1954.** The calculation of formation curves of metal complexes from pH titration curves in mixed solvents. *J. Chem. Soc.* 2904-2909
15. **Reid E. W. & Hofmann H. E.1929.** 1, 4-Dioxan. *Industrial & Engineering Chemistry.* **21**: 695-697
16. **Vogel A. I. 1956.** A textbook of practical organic chemistry, Longmans, London. **3rd edition**: 177
