International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 076 Published Mar. 2018
Volume No. 04, Issue No.08, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: Mixed Metal Complexation study of …

Mixed Metal Complexation study of Transition series with Thiourea and Alanine

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Abstract: Mixed metal complexation study of transition metal ions of some transition metals like Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with Thiourea as secondary ligand whereas Alanine as primary ligand has been evaluated by the potentiometric technique at 25±0.1°C and 0.1M (NaClO4) ionic strength.The protonation constants of the ligand were calculated from the potentiometric pH titrations data of solutions according to Irving and Rossetti's method.

Keywords: Stability constant, Thiourea, amino acids, pH metry, mixed ligand complexes

Introduction: Pharmacologically active compounds contend various functional groups in its structure, which is able to bind metal ions present in living organisms. Mixed Metal complexes of biomolecule are found to be more effective than originalbiomolecule. Many researchers attracts towards mixed metal complexation study of pharmacologically active compounds due to its application in medicinal study. Mixed metal complexation of medicinal drugs play vital role in the bio - chemical activity[1-3]. It is used in different areas, such as biological processes, pharmaceuticals, separation techniques, analytical processes etc.

Amino acids are the structural unit of proteins. These are essential constituents of all living cells and contain one or more amino and carboxylic groups and have good coordination sites for the metal complexation. Thiourea is an organosulpher compound used as reagent in organic synthesis whereas its derivatives are used as organocatalyst. So in present study we had planned and executed metal complexation study of Thiourea and alaninewithtransitionmetalions.

In the present investigation the formation and stability of ternary mixed metal complexes containing Thiourea (N.S) donor secondary ligands with alanine (N,O-)Donor primary ligands (fig.1) are reported at 25±0.10C in 0.1 M (NaClO4). The effect of the substituent on the dissociation constants, and on the stability & formation ofthe binary and ternary complexes have been evaluated by comparing the relevant data for systems containing determined under identical experimental conditions.

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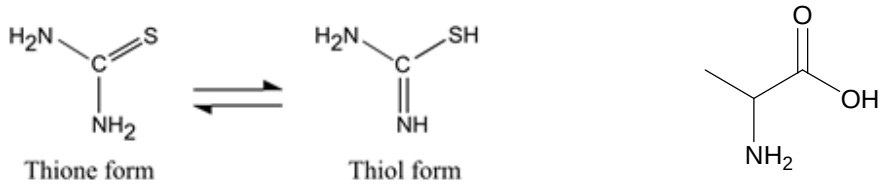

Thiourea **Alanine**

Fig.1: Structure of Compounds

Experimental Section:

Materials and solution:Thiourea was of analytical grade and NaOH, NaClO4, HClO4 and copper salt were of local grade. The solutions used in the potentiometric titrations were prepared in double distilled water. The NaOH (0.041M) solution was standardized against oxalic acid solution (0.1M) and the standard alkali solution was again used for standardization of HClO4. The copper salt solution was standardized using EDTA titrations [4]. The ligand (NA) is soluble in double distilled water. The pH meter was calibrated before each titration with standard buffer solutions of 4.00, 7.00, and 9.2. The pH-meter (ELICO, L1-120) was used with a combined glass electrode assembly.

Potentiometric Procedure:

In this study of binary and ternary chelates by the potentiometric titration technique. The following sets were prepared in the standard:

(1)Free HClO4
(2)Free HClO4 +Ligand (LP)
(3) Free HClO4 +Ligand (LP) +Metal ion
(4)Free HClO4 +Ligand (LS)
(5) Free HClO4 +Ligand (LS) +Metal ion (M)
(6) Free HClO4 +Ligand (LP) +Ligand (LS) +Metal ion (M)

Against standard sodium hydroxide, the ionic strength of solutions was maintained constant by adding appropriate amount of (0.1M) Sodium perchlorate solution. The titrations were carried out at room temperature in inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrode to keep out CO2 by noting the pH of precipitation for ML_P, ML_S and ML_PL_Stitration, the formation of mixed ligand complexes can be concluded.

Calculations:

The protonation constants of the ligand were calculated from the potentiometric pH titrations data of solutions accordingto Irving and Rossetti's method [5]. For this purpose, theaverage proton-ligand formation number (na)at various pHfor the ligand was determined according to the literature [6]. The value of pKa was read directly from na= f (pH) graph atna=0.5. For the calculation of stabilityconstants of binarycomplexes (using the potentiometric titration data of thesolutions and according to Irving and Rossotti's method [5],the metal-ligand (M-NA and M-2NA) formation

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number(n-) at various pH for the ligand was determined according to theliterature [6]. Then pL values were calculated with using the equation from the literature [6].Having thus obtained corresponding values of n- and pL, the formation curve of the metal-ligand system is drawn and the stability constant isread directly at n-= 0.5 , 1.5. The calculation of the stability constant of ternary complex by the stepwise equilibria in solution would be confirmed when the mixed ligand curve could besuperimposed over the binary MLp or MLs titration curve. The method of Thomson and Loraas [7] for calculation of stepwise stability constants is widely used.

RESULTS AND DISCUSSION:

Schwarzenbech and Ackermann [8] found that the stability of chelate decreases as the size of ring increases. Mellor &Maley [9] 50% Dioxane-Water medium. The order of stability was: Pa > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg

Irving – William [10] have correlated their data by plotting the stability constant against the atomic number of the metal ion. The order is, Mn < Fe < Co < Ni < Cu < Zn

In complexation Thiourea is used as one of the ligand, along with secondary Alanine. The potentiometric Celvin Bjerrum method is used as discussed in the experimental section. The metal ligand stability constants for binary as well as ternary are determined .The protonation of Thiourea and Alanine was determined by half integral method. The protonation constant of Thiourea and Metal-ligand satability constant are shown in **Table 1.**

Table1. Protonation constant of Thiourea and Metal-Ligand Stability

Metal	Thiourea Stability Constant(logK1)
Fe(III	3.892
Co(II)	3.8142
Ni(II)	3.986
Cu(II)	3.674
Zn(II)	3.4123

The stability parameters of ternary complexes of Thiourea with Alanine and transition metal ions like Fe, Co, Ni, Cu, Zn.

The logK values for these are given in **table 2.**

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Table 2: A Complexometric parameters of ternary complexes of Thiourea With Alanine as Secondary ligand

Metal ion	Mixed Ligand	$LogK_{MXY}$
Fe(III)	Thiourea + Alanine	10.527
Co(II)	Thiourea + Alanine	10.580
Ni(II)	Thiourea + Alanine	10.572
Cu(II)	Thiourea + Alanine	10.657
Zn(II)	Thiourea + Alanine	10.854

The order of stability constant of ternary complexes of Thiourea and alanine were found to be Zn < Cu < Ni < Co < Fe.

CONCLUSION: The present work describes the complex formation equilibria of transition metal ions with Thiourea and alanine. The effect of ligand properties on the stability of the complexes was investigated. The metal complexes of Thiourea may be improving its application in textile industry as well as role of organocatalyst in several organic syntheses. This would require specially designed research conducted by specialized organic chemist.

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