ISSN 0973-3450 (Print)
JUC Vol. 12(3), 71-74 (2016). Periodicity 2-Monthly
ISSN 2319-8036 (Online)

JOURNAL OF ULTRA CHEMISTRY
An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering
website:- www.journalofchemistry.org
Estd. 2005

pH metric Investigation of Complexation of 3,5 Dinitro salicylic Acid (DNS) with transition metal ions

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http://dx.doi.org/10.22147/juc/120303

Acceptance Date 21st Oct., 2016, Online Publication Date 2nd Nov. 2016

Abstract

The stability constants of metal complexes of DNS with transition metal ions have been evaluated pH metrically in aqueous solution at 27° C temperature and 1N ($NaNO_3$) ionic strength. Protonation constant and formation constant were determined by using Irving Rossoti titration method. Metal ligand ratio was 1:2. In order to find out the relationship between stability constant and physical properties of the metal ions regression analysis was performed using Origin profession 6.0 programme.

Key words : Dinitro salicylic Acid, metal ions, pH metric.

Introduction

To understand the complex formation ability of the ligands and the activity of complexes, it is essential to have the knowledge about solution equilibria involved in the reactions. The extent to which the ligand binds to metal ions is normally expressed terms of stability. A survey of literature reveals that studies on complexation of DNS are very scarce, therefore study was undertaken in continuation with our earlier studies[1].

Dinitrosalicylic acid, chemically known as 3,5-dintrosalicylic acid, is a yellow solid compound. The molecular formula is $C_7H_4N_2O_7$. Dinitrosalicylic acid is soluble in water. DNS also used as pharmaceutical intermediate. This acid finds application in biochemistry or medical sciences, to detect reducing substances in urine and for measuring the quantities of carbohydrates levels in blood. Majorly used in assay of alpha-amylase, this acid is widely applicable for enzymatic methods.

Experimental

All the chemicals used of high purity. Ligand sample was of SD Fine AR grade. All the solutions were prepared in double distilled water. All the

solutions were standardized before use by known methods. Metal nitrates were used due to their high solubility in water. 1N($NaNO_3$) for maintaining ionic strength. Glass electrode with digital potentiometer (ELICO LI-20) was used for pH measurement. pH meter was calibrated using buffer solution of pH = 4 and pH = 7 before titration. The experimental procedure involved three titrations (I) HNO_3 (A) (II) HNO_3 + Ligand (A + L) (III) HNO_3 +Ligand + metal (A + L + M) against 0.2 N NaOH.

The results obtained for each titration was plotted as a volume of NaOH vs. pH and related volume at succeeding pH determined and calculated.Proton ligand and metal ligand stability constant were determined by using excel computer programme.

Results and Discussion

The observed pH values from above three titrations are then plotted against the volume of alkali added. Three titration curves are obtained (Figure 1), corresponding to the titrations mentioned in the experimental part. The titration curves were separated from each other each taking approximately S shape. The end point for the titration increased in the order I > II > III. The maximum value of *n* did not exceed two for all complexes indicating the formation of 1:1 and 1:2 complexes.

Considerable separation of metal complexes curve from reagent curve along volume axis is an evidence for complex formation. The use of very dilute solution ruled out the possibility of formation of polynuclear complexes.

Average numbers of protons associated with ligand were calculated from acid and ligand titration curve and used to get pKa values. From table 1 it is clear that DNS has the highest pK_2 value due to -OH group and lower pK_1 value due to carboxylic group. The pKa values obtained by half integral and point wise method are in agreement. $\overline{n}_A$ Vs. pH plot was obtained between 0-2 indicating that the ligand has two dissociable protons. The maximum value of *n* obtained was 2 indicating the formation of 1:1 and 1:2 complexes (figure 2).

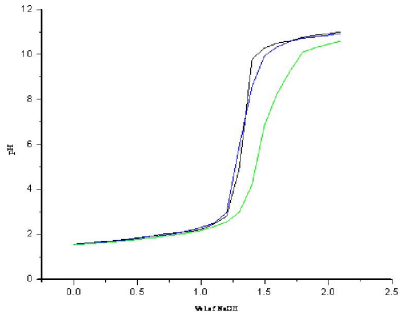

Figure 1 titration curve

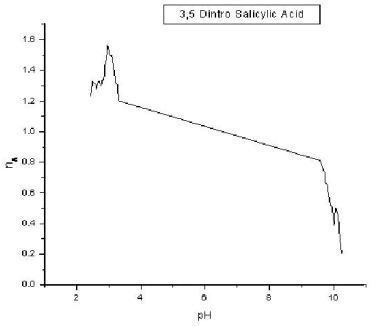

Figure 2 proton ligand formation curve

Table 1. Stability constants of DNS (1:2)

pK_H	Metal ion	Log K_1	Log K_2	Log **β**
a) pK_1=2.9441	**Cu** (II)	5.8084	3.8419	9.6503
	Ni (II)	4.2998	3.8440	8.1439
a) pK_2=9.9425	**Fe** (III)	4.1094	3.8639	7.9733
b) pK_1=2.6270	**Cd** (II)	3.7524	-	3.7524
b) pK_2=9.8880	**Co** (II)	3.4469	-	3.4469
	Zn (II)	-	-	-

a = Half integral, b = Point wise

DNS is a bidentate ligand, it has two binding sites phenolic –OH which has higher pKa and –COOH having lower pKa. Under the present experimental condition, the protonation constant obtainedare 2.944 and 9.888. The value of 2.944 is due to –COOH group. This value is low as compared to the carboxylate group (4.2) in the normal cases; the decrease in pKa value may be due to electron withdrawing effect exerted by two nitro groups.The Metal-ligand stability constant for M+DNS system are shown in the table 1. The values of Proton ligand constant (pKa) obtained are

in agreement with literature values. Some variations may be due to different experimental condition. The order of stability values reported are in agreement with the literature reported [2-5]. For the present investigation the order of stability found to be Cu(II) > Ni(II) > Fe(III) > Cd(II) > Co (II) for 1:2 complexes.

Merce *et al*.[2] compared stabilities of salicylic acid with its nitro derivatives. They reported DNS more effective chelating agent than salicylic acid(SA) itself, the ligands are not bulky and can provide sight to the complex formation. The pKa values reported by them are 7.08 and 9.83 for DNS and 5 Nitro Salicylic Acid (NSA) respectively; reported high stability for Copper complexes of DNS and NSA as 7.2, 4.2. Dube and Dhindsa[3] worked on complexes of DNS with different metal ions and reported formation of 1:1 complexes, the order of stability reported by them is Cu(II) > Ni(II) > Co(II) > Zn(II) >Mn(II). Salicylic acid (SA) has pKa values as 2.84 and 13.66 [4]. Abd Gaber *et al*.[5] studied the complexes of derivatives SA with nontransition metal ions in aqueous medium. The pKa values found are 1.31, 7.00 and 2.49, 12.00 for DNS and 5-sulpho salicylic acid respectively. Decrease in pKa may be due to attachment of two electron withdrawing nitro groups in case of DNS. They reported the high stabilities for Copper and Nickel complexes. pKa value for benzoic acid 4.20 and phenol 10.00 are reported in literature[5]. Shelke and Jahagirdar[6] worked on neodymium complexes of phenolic acids and reported high stability constant values 3.33, 14.20 for 4-hydroxy salicylic acid and formation of 1:1 complexes. Faraji *et al*.[7] reported pKa values of salicylic acid and 5-nitro salicylic acid in ethanolic medium as 2.916 and 2.017 respectively.

A linear regression analysis of stability constant of complexes against physical properties of metal ions has been carried out considering the equation y = Bx + A. The regression coefficient r is calculated using computer software Origin 6.0. These are shown in table 4. The physical properties which are considered in the present study is given in the table 3. It was observed that none of the physical property of the metal ion shows above 0.9 regression coefficient for stability constant of metal ligand complexes.

Ionization potential (I.P.) is one of the important properties of metal ions. For present work second I.P. was considered. It was observed that in case metal DNS complexes, a positive Correlation obtained for atomic mass, I. P., atomic radius, electronegativity.

Table 3. Physical properties of metal ions

Metal ion	At.no.	I.P. kJ/mol	Ion.rad pm	Elect.	At.wt.	At.rad pm
Fe	26	1561	64	1.64	55.85	126
Co	27	1648	74	1.70	58.93	125
Ni	28	1753	72	1.75	58.71	128
Cu	29	1958	69	1.75	63.54	128
Zn	30	1733	74	1.66	65.38	138
Cd	48	1631	109	1.46	112.4	154

Table 4. Correlation coefficient for stability constant vs. physical properties of metal Ligand

Atomic number	Atomic mass	I.P. KJ/mol	Atomic radius (ppm)	Ionic radius (ppm)	Electrone-gativity
0.256216	0.519281	0.774399	0.519281	0.028713	0.418349

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